Final Report

Selenium in San Francisco Bay

Conceptual Model/Impairment Assessment

Prepared by:

Khalil Abu-Saba, Ph.D. and **Scott Ogle, Ph.D.**

Larry Walker Associates ***Pacific EcoRisk***

Prepared for:

Clean Estuary Partnership

June 2005

Executive Summary

Background Information

Section 303(d) of the Clean Water Act requires states to identify water bodies not attaining water quality standards (i.e., waters whose beneficial uses have been impaired), to identify the pollutant causing the impairment, and to develop total maximum daily loads (TMDLs) that will reduce and eventually eliminate the impairment and restore the beneficial use(s). In response to observations of elevated concentrations of selenium in the tissues of diving ducks, the CA Department of Health Services (DOHS) issued health advisories against the consumption of the ducks; these advisories reflect an impairment of San Francisco Bay's beneficial uses, and served as the basis for the San Francisco Bay Regional Water Quality Control Board (Regional Board) to place 6 San Francisco Bay water bodies on the 303(d) list as being impaired due to selenium in 1998:

1. Sacramento-San Joaquin Delta,
2. Suisun Bay,
3. Carquinez Strait,
4. San Pablo Bay,
5. Central San Francisco Bay,
6. South San Francisco Bay.

More recently, the Bay Protection and Toxic Cleanup Program (BPTCP) identified 5 Bay water bodies as Category IV sites (i.e., locations having elevated chemicals in sediments *and* adverse biological impact as indicated by either sediment toxicity *or* degradation of the benthic community):

1. Castro Cove,
2. Central Basin,
3. San Leandro Bay,
4. Oakland Inner Harbor (Pacific Drydock Yard 1),
5. Oakland Inner Harbor (Oakland-Fruitvale).

If the observed sediment toxicity at these BPTCP sites is, in fact, due to selenium, then several of the Bay's beneficial uses, in addition to the previously-mentioned commercial and sport fishing, would be impaired due to elevated selenium. As a result, the State Water resources Control Board (State Board) placed these sites on the 303(d) list in 2002.

A Conceptual Model for Selenium

The conceptual model of the fate and effects of selenium in the San Francisco Estuary watershed integrates information on the sources and loading of selenium to the Bay, the chemical characteristics of selenium, and the linkages between these and the resultant cycling and bioaccumulation of selenium. Because selenium occurs in a wide variety of different chemical forms, a normal discussion of "cycling" processes can rapidly become overly complex. As a result, discussion of cycling processes in this report is limited to those involved in selenium bioaccumulation.

Like mercury, selenium is a naturally-occurring trace element. And like mercury, many of the problems that selenium can cause in aquatic ecosystems result from:

1. mobilization of selenium from terrestrial sources into surface waters,
2. transformation of inorganic forms into organic forms, and
3. bioaccumulation of these organic forms into higher trophic level organisms.

Selenium occurs in several different chemical forms or *species*:

- **selenate** (SeO_4^{+2}), the most stable form in most oxic waters,
- **selenite** (SeO_3^{+2}), often abundant due to slow conversion to selenate, selenite is rapidly taken up by microbes and algae, and is readily biotransformed into organic forms,
- **elemental selenium** (Se^0), least bioavailable of major selenium forms, but important due to formation in sediments,
- **inorganic selenide(s)** (e.g., metal-Se^{-2}), potential loss mechanism via precipitation with metals,
- **organoselenides** (R-Se^{-2}), occurs as wide variety of compounds, including selenomethionine, one of the most bioavailable and toxic forms.

Sources and Loading - The three major sources of selenium to the Bay are:

1. the Sacramento River,
2. the San Joaquin River, which includes seleniferous agricultural drainwater,
3. discharges from oil refineries,

all of which bring selenium into the northern reach of the Bay system. The southern reach of the Bay does not have similar tributary or industrial discharge sources, and acts much more like a tidal lagoon; POTWs are the major sources of selenium to South Bay.

The **Sacramento River** is the largest source of surface water runoff into San Francisco, and the concentrations of total dissolved selenium in the Sacramento River water have remained essentially unchanged over the past 20+ years.

The **San Joaquin River** concentrations of total dissolved selenium in the San Joaquin River are much higher than in the Sacramento River. As state-mandated increases in the flow of San Joaquin River water to the Delta and Bay come into play, the contribution of the San Joaquin River to northern San Francisco Bay can be expected to increase.

Studies in the 1980's had identified **oil refinery discharges** as being a major source of selenite to the Bay. Since that time, the refineries have achieved an average 66% reduction in total dissolved selenium discharge, and a remarkable 92% average reduction in the selenite being released. Selenite concentrations, particularly in the Suisun Bay-Carquinez Strait-San Pablo Bay region, have decreased by 82%, roughly the same decrease as that in the refinery effluents.

Sources of Suspended Particulate Selenium **-** The primary source for selenium bioaccumulation at the lower trophic levels is ingestion of particulate materials (i.e., microbes, algae, detritus, as well as abiotic particulate materials). Studies have indicated that particulate selenium consists of resuspended Bay and Delta sediment and cellular (microbial and algal) organoselenides, and it was concluded that particulate selenium is a function of phytoplankton productivity and riverine inputs of sediment.

Selenium Cycling and Bioaccumulation - While dissolved selenium species can cause direct toxicity to aquatic organisms, the lethal threshold concentrations (i.e., LC_{50} values) are typically much, much higher than the waterborne concentrations seen in all but the most contaminated of ecosystems. This is one reason why water quality criteria are typically many orders of magnitude higher than the concentrations measured in the San Francisco Estuary's ambient waters.

However, the reproductive and other health impairments that can result from *bioaccumulation* of selenium up through the food chain can be a toxicity issue of 'real world' concern, as evident by the DOHS health advisories and the observation of waterfowl and fish reproductive problems at Kesterson and elsewhere.

***The Bioaccumulation and Biotransformation of Dissolved Selenium* -** Microbes and algae comprise the "base" of the food chain, and perform the most critical selenium biotransformation step: the reduction of selenite and selenate and incorporation of the reduced selenides into seleno-amino acids, particularly *selenomethionine*, an analog to the essential amino acid methionine (due to its chemical similarity, the selenium is 'mistakenly' used in place of sulfur in the synthesis of this compound); selenomethionine is believed to be the major cause of much of the observed reproductive problems in fish and waterfowl.

Studies have indicated that selenite uptake by **marine bacteria and algae** is rapid, and that selenite is rapidly biotransformed into seleno-amino acids and proteins, whereas the uptake and biotransformation of selenate is much more limited, indicating significant differences in the cycling, fate, and effects of selenite vs. selenate.

Studies have also indicated that selenium concentrations in algae did not increase proportionately to 30-fold increases in ambient selenite from 0.15 to 4.5 nM, suggesting that the algal tissue concentrations of selenium in San Francisco Bay may have been relatively unaffected by the recent reductions in the Bay's ambient water selenium concentrations.

***The Bioaccumulation of Selenium by Invertebrates* -** It has long been recognized that assimilation of ingested selenium (i.e., from the diet) is the primary mechanism for bioaccumulation of selenium by invertebrates. Studies with **zooplankton** have indicated that the assimilation of selenium from algal diets are very high, although the zooplankton do not accumulate selenium to concentrations much higher than present in their microbial/algal diet. Recent studies of selenium in San Francisco Bay zooplankton reported that the zooplankton tissue concentrations were generally similar to those found in other "uncontaminated" systems, although the observation of markedly higher concentrations in the Fall of 1999 that coincided with a peak concentration in particulate selenium suggests that zooplankton in the Bay may be subject to occasional increases in selenium content.

Unlike zooplankton, **bivalves** have been observed to accumulate ingested selenium to concentrations markedly higher than in their particulate diet, in part due to their high assimilation rates of the selenium, but also to their relatively low excretion rates. This difference is most dramatic in the Asian clam ***Potamocorbula amurensis***, an exotic species that invaded San Francisco Bay in the mid 1980's and has since become the dominant benthic organism in much of the Bay; *P. amurensis* accumulates selenium to much higher concentrations (e.g., 6-20 μg/g, dry wt) than either zooplankton or other bivalves.

***Selenium Bioaccumulation by Fish and Waterfowl* -** Given that *Potamocorbula amurensis* tissue selenium concentrations can be so elevated, it is not surprising that the higher trophic level organisms that eat these bivalves will, in turn, exhibit elevated tissue selenium concentrations. In fact, the elevated selenium concentrations in the Greater Scaup and Surf Scoter that triggered the initial health advisories which led to the current 303(d) listing almost certainly reflect the fact that clams are important food items for these diving ducks. Similarly, *P. amurensis* is a dominant food item for white sturgeon and mature Sacramento splittail, which are the Bay fish species exhibiting the highest tissue selenium concentrations.

In contrast, fish that feed primarily upon the planktonic food chain (i.e., such as juvenile striped bass feeding on zooplankton and other water column organisms) do not exhibit similarly elevated tissue selenium concentrations.

What is Driving Selenium Bioaccumulation in San Francisco Bay?

Interestingly, while the concentrations of total dissolved selenium, and more importantly, of selenite, declined dramatically in the late 1990's, there have been no reported corresponding reductions in the reported *P. amurensis* tissue concentrations. This is likely due to the fact that it is the ingestion and assimilation of particulate selenium that drives bioaccumulation by *P. amurensis*, and in similar contrast with the declining selenium concentrations in the Bay's water, <u>there has been no decline in the selenium concentrations of the suspended particulate material</u>.

Given the magnitude of the decline in dissolved selenium between and 1997-1999, it seems as though there should be *some* measurable change in particulate selenium … however, none was observed. This, of course. raises the question:

> **"Why hasn't the selenium concentration of suspended particulates (and the corresponding selenium concentration in the bivalve *P. amurensis*) declined in response to the declines in dissolved selenium in the Bay?"**

Upstream riverine and Delta sediments and Delta primary productivity are major sources of the suspended particulate selenium. Delta sediment selenium concentrations are actually higher than those in the northern reach of the Bay, and the selenium concentrations are generally constant with depth. This suggests that the reservoir of upstream sediments provides a steady supply of particulate material (suspended and bedded) to the northern reach of San Francisco Bay with consistent concentrations of selenium that will be independent of the Bay's dissolved selenium concentrations, and therefore, unaffected by the reductions in selenium that were affected by the oil refineries.

The absence of any reduction in particulate selenium might also be explained by the selenium uptake of the phytoplankton component. Algal uptake studies have indicated that the algal selenium concentrations did not increase proportionately to varying selenite concentrations over a 30-fold range that encompasses the concentrations found in the Bay. This suggests that algal selenium bioaccumulation is not proportional the Bay's dissolved selenium concentrations (at the range of concentrations that have been observed in the Bay), and therefore, may be relatively unaffected by the reductions in selenium that were affected by the oil refineries.

Impairment Assessment: Current Conditions

Compliance with Water Quality Objectives - Examination of the waterborne selenium concentrations reported by the Regional Monitoring Program (RMP) reveals that there have been no exceedances of the U.S. EPA and the California Toxics Rule criteria; indeed, the ambient concentrations of selenium in the Bay's waters are typically orders of magnitude below the criteria levels.

Compliance with Sediment Quality Objectives - There are no existing sediment criteria for selenium. US Fish & Wildlife Service selenium experts have established 4 μg/g, dry wt, as the maximum allowable selenium concentration in their guidance for TMDLs. The sediment selenium data reported by the RMP indicate that the sediment concentrations in the Bay are typically much lower than this guidance threshold.

Health Advisory Against Consumption of Resident Organisms - The CA DOHS has provided the following health advisory warning for inclusion in the CA Dept. of Fish & Game Waterfowl Hunting Guidelines:

> <u>Suisun Bay (Contra Costa and Solano Counties)</u>
> <u>San Pablo Bay (Contra Costa, Marin, Solano, Sonoma Counties)</u>
> Because of elevated selenium levels, no one should eat more than 4 oz. per week of scaup meat, or more than 4 oz. of scoter meat in any 2 week period. No one should eat livers of duck from the area.
>
> <u>San Francisco Bay (Alameda, Contra Costa, Marin, San Francisco, San Mateo, Santa Clara Counties)</u>
> Because of elevated selenium levels, no one should eat more than 4 oz. per week of Greater Scaup meat from the central bay, or more than 4 oz. of Greater Scaup meat from the South Bay in any 2-week period. No one should eat livers of duck from the area.

Bay Protection Toxic Cleanup Program Toxicity - Based upon the weight-of-evidence presented in this Impairment Assessment, it is concluded that selenium is ***not*** impairing the BPTCP sites that were added to the 303(d) list in 2002.

Assessment of Impairment by Selenium - Any assessment of impairment of the Bay's waters will by necessity be based upon a "weight of evidence" approach, with review and evaluation of all available relevant information. The Clean Estuary Partnership (CEP) has proposed a set of potential conclusions and outcomes of impairment assessment that reflects the

State's 303(d)-listing policy categorizations. Based upon this current review of available information, it is this study's conclusion that:

> **There is *possible impairment* of the Bay by selenium –** The continued presence of a health advisory against the consumption of diving ducks in San Francisco Bay clearly meets the State Board's Category 4 classification that selenium does impair one or more of the beneficial uses of San Francisco Bay. However, there are some uncertainties that must be addressed with additional studies. As a result, it must be concluded that there is **possible impairment** of San Francisco Bay by selenium.
>
> However, it is concluded that there is **no impairment** of the BPTCP sites by selenium, and de-listing of these sites is warranted.

Uncertainties and Data Gaps

Any objective analysis will always contain uncertainties. A summary of uncertainties is an important component of the impairment assessment, as the uncertainties guide subsequent investigations. Uncertainties with the assessment of impairment by selenium identified and discussed in this report include:

- Appropriate calculation of dietary exposures,
- Potential impairment of other ecological receptors,
- Compliance with proposed and/or planned water quality criteria,
- Future loadings of agricultural drainwater.

Where Do We Go From Here: Filling the Information Gaps

This report concludes with identification of some potential future projects to obtain additional data and conduct more analysis of the sources, fate, transport, and effects of selenium. In other documents or forums, the CEP will develop appropriate strategies for addressing selenium in the Bay and its watersheds. These strategies may include:

- Data collection or analysis,
- Implementation of corrective actions,
- Formulating and refining management questions and setting priorities for the above 2 activities,
- Determining an ongoing process for integrating all of the above.

There may be control measures, remediation, and regulatory actions that can and should begin now, even with existing uncertainties. The CEP partners are committed to identifying these actions. Future CEP data gathering and technical analysis should focus on determining the potential effectiveness, and actual effects, of actions to reduce or eliminate impairment and to restore beneficial uses of the Bay.

Table of Contents

Appendices

List of Figures

List of Tables

Page

1. Introduction

Section 303(d) of the federal Clean Water Act (CWA) requires states to identify those water bodies not attaining water quality standards (i.e., waters whose beneficial uses have been impaired), to identify the pollutant causing the impairment, and to develop remediation plans (known as “total maximum daily loads”, or TMDLs) for each pollutant in each water body that will reduce and eventually eliminate the impairment and restore the beneficial use(s). In response to observations of elevated concentrations of selenium in the tissues of diving ducks, the CA Department of Health Services (DOHS) issued health advisories against the consumption of the ducks. These health advisories reflect an impairment of San Francisco Bay’s beneficial uses, which is the basis for the San Francisco Bay Regional Water Quality Control Board (Regional Board) to identify much of San Francisco Bay as 303(d)-listed “impaired water bodies” due to selenium contamination.

In the almost 20 years that have passed since the initial health advisories were issued, there have been significant changes in the loading and fate and effects of selenium in San Francisco Bay, and the management responses to new information, as it has become available, would be a textbook example of adaptive environmental management. Two decades ago, resource agencies were finding dead and deformed baby birds in Kesterson Reservoir resulting from the disposal of subsurface agricultural drainage from the western San Joaquin Valley. Monitoring of selenium in ducks, fish, and invertebrates in the Bay and Delta revealed levels that could cause health risks to people and wildlife. By 1989, studies had identified local industrial selenium sources to the Bay, and the Regional Board required those sources to reduce selenium discharges. All of this took place amid an invasion of the Asian clam (*Potamocorbula amurensis*), an exotic species that is very efficient at moving selenium into the food chain. Now, six years after significant selenium load reductions have been implemented by Bay Area oil refineries, and before long-term plans to manage agricultural drainage in the Central Valley are finalized, it is a good time to review the original basis for concern over selenium in the Bay, and summarize new information that has surfaced over the past decade.

This report includes a brief narrative of the 303(d)-listing history, followed by a conceptual model and a current impairment assessment for selenium in San Francisco Bay. The conceptual model describes the sources of selenium to the Bay and the processes that determine the occurrence and concentrations of selenium in the system. The impairment assessment re-evaluates the rationale for the initial 303(d)-listing(s) and summarizes existing data on selenium in San Francisco Bay. Because there have been significant changes in the sources and loading of selenium over the past 10 years, an important part of this document is the assessment of recent studies that may significantly affect how we think selenium behaves in the Bay, and recent and ongoing regulatory developments that may affect compliance with regulatory criteria and the potential impairment of San Francisco Bay by selenium.

This report has been produced for the Clean Estuary Partnership (CEP). The CEP is a collaboration of the Bay Area Clean Water Agencies, Bay Area Stormwater Management Agencies Association, and the San Francisco Bay Regional Board. Other important participants include the San Francisco Estuary Institute, Clean Water Fund, San Francisco Bay Keeper, Port of Oakland and the Western States Petroleum Association. This cooperative partnership facilitates efforts to improve water quality in San Francisco Bay by providing financial and staff support for technical studies, discussion of management questions and strategies, and stakeholder outreach activities.

Several Conceptual Model/Impairment Assessment (CM/IA) reports have been commissioned by the CEP for pollutants that have been identified in the past as possible causes of impairment to beneficial uses in San Francisco Bay. The general objectives of these CM/IA reports are:

- Develop a conceptual model that describes the current state of knowledge for the pollutant of concern, including sources, loads, and pathways into and out of the Bay and its water, sediment and biota;
- Evaluate the current level of impairment of beneficial uses, including description of standards or screening indicators and relevant data;
- Recommend options for the next steps needed to reduce uncertainties in the conceptual model and impairment, to assist the CEP partners in balancing priorities for data gathering along with other pollution prevention activities.

Since the state of knowledge varies among pollutants, initial CM/IA reports may lack the resources to fully achieve all these objectives in each case. This CM/IA report should be viewed as a tool for planning and an important step in resolution of selenium-related issues, and not as a conclusive statement on the conceptual model, beneficial use impairment, or next steps needed to resolve selenium-related issues.

This report is a planning document. At the end, key findings are expressed as management questions that may lead to either study plans or action plans, depending on the level of certainty about the answers. The report is also intended to be a tool for communications and outreach, so it relies on graphics, conceptual logic, and plain language to explain what we know and what we need to know about how watershed management in California affects selenium in the food chain and the health of people and wildlife who eat fish and invertebrates from the Bay.

2. Background Information: the 303(d) Listing

2.1 San Francisco Bay

San Francisco Bay is the largest estuary on the West Coast of the United States, draining an overall watershed area of 60,000 square miles (Figure 1), and the Bay's deepwater channels, tidal mudflats and wetlands, and freshwater streams and rivers provide a wide variety of important ecological habitats. The Sacramento and San Joaquin Rivers enter the northern reach of the Bay via the Delta, at the eastern end of Suisun Bay (Figure 2), and contribute almost all of the freshwater flow into the Bay, although there are many smaller tributary rivers and streams within the Bay's immediate watershed. Suisun Bay, which is the largest brackish-water marsh in the United States, flows through the Carquinez Straits into San Pablo Bay. The South Bay, at the other end of the Bay system, receives much less freshwater inflow than does the northern reach, and acts more like a tidal lagoon. The northern and southern Bay segments meet in the Central Bay, which is the Bay's connection to the Pacific Ocean, and which is heavily influenced by oceanic conditions.

2.1.1 The Impaired San Francisco Bay Segments and Water Bodies

The San Francisco Bay segments or water bodies that are currently listed as being impaired by selenium (Figure 2) are listed in Table 1.

Table 1. The San Francisco Bay segments or water bodies that are currently on the Clean Water Act 303(d) List as being impaired by selenium

Bay Segment or Water Body	1998 303(d) List	2002 303(d) List
Sacramento-San Joaquin Delta	X	X
Suisun Bay	X	X
Carquinez Strait	X	X
San Pablo Bay	X	X
Central San Francisco Bay	X	X
South San Francisco Bay	X	X
Central Basin (part of Central SF Bay)		X
Castro Cove		X
Oakland Inner Harbor – Pacific Dry Dock (part of Central SF Bay)		X
Oakland Inner Harbor – Fruitvale (part of Central SF Bay)		X
San Leandro Bay		X

In general, little is known about concentrations of selenium in the Baylands, margins, and salt marshes bordering the Bay.

Figure 1. The San Francisco Estuary watershed, including the Sacramento River watershed and the San Joaquin River watershed in the Central Valley, and the San Francisco Bay watershed.

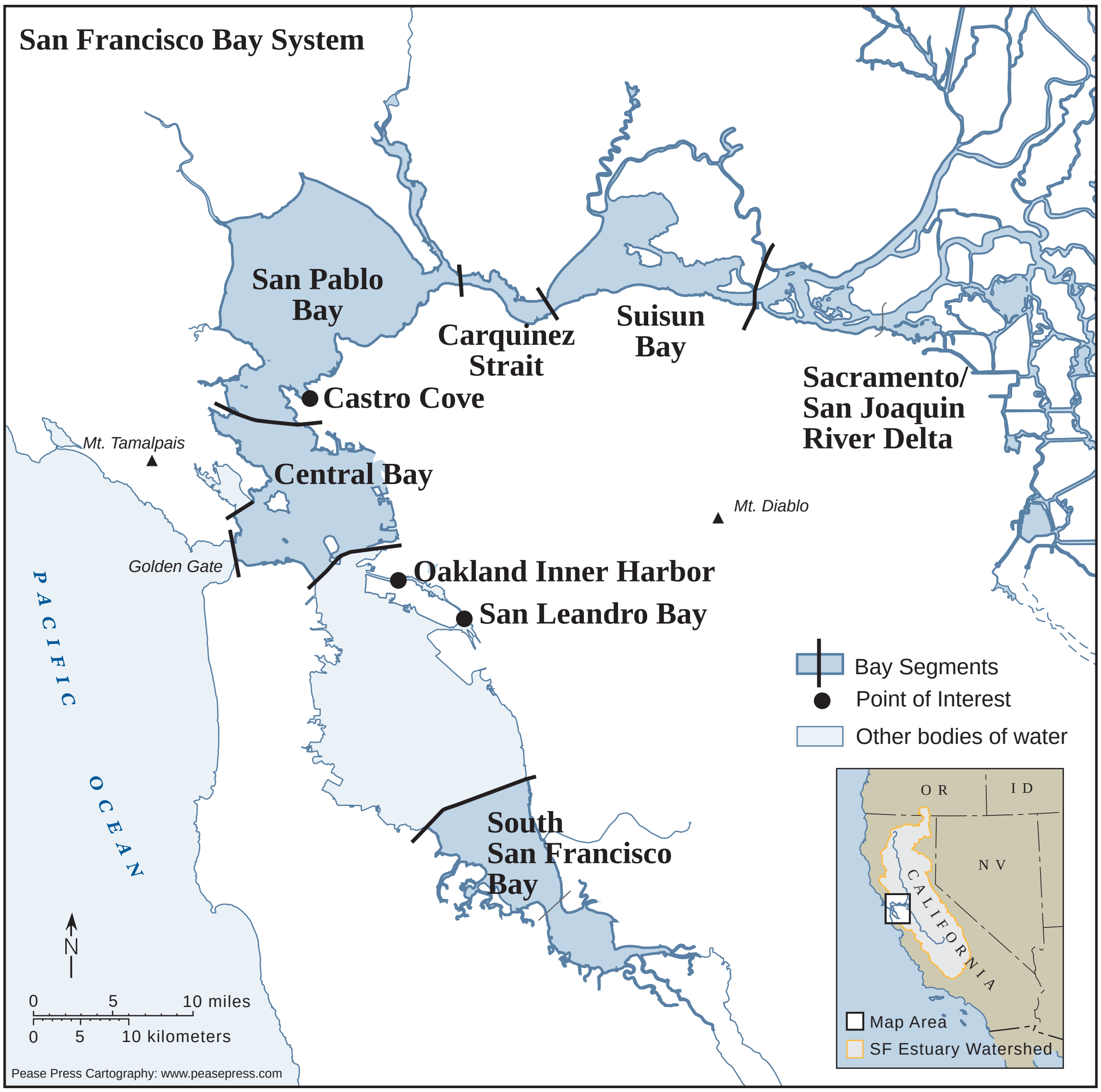


Figure 2. The San Francisco Bay system, including the segments and water bodies of the Bay that have been placed on the 303(d) list for impairment by selenium.

2.2 Regulatory Background for the 303(d) Impairment Listing

Section 303(c)(2)(a) of the federal Clean Water Act requires that states develop water quality standards to protect human health and the environment, and Section 303(d) requires that states develop lists of water bodies that do not meet those standards.

In California, the Porter-Cologne Water Quality Control Act, which is contained in the California Water Code, identifies the State Water Resources Control Board (State Board) and Regional Water Quality Control Boards (Regional Boards) as the principal agencies responsible for controlling water quality in California. This joint agency responsibility couples state-level coordination with regional familiarity with local conditions. Accordingly, the San Francisco Bay Regional Board has the responsibility for regulating and protecting water quality within the San Francisco Bay region, which it addresses within its basin-specific Water Quality Control Plan (Basin Plan). The key elements of the San Francisco Bay Basin Plan consist of:

- A statement of the beneficial uses of San Francisco Bay that are to be protected;
- Identification of the water quality objectives needed to protect these beneficial uses;
- An implementation plan to protect these beneficial uses, primarily via regulation of discharges to the Bay and its tributaries (SFBRWQCB 1995).

In meeting the requirements of the Clean Water Act, and consistent with the Basin Plan, when water quality objectives are not being met such that any one or more of the Bay's beneficial uses are impaired, the San Francisco Bay Regional Board is responsible for placing the impaired body of water on the 303(d) list, with the listing being subject to approval by EPA. In complying, the San Francisco Bay Regional Board has developed successive lists of "impaired" segments or water bodies since 1976. The State Board has subsequently issued the *Water Quality Control Policy for Developing California's Clean Water Act Section 303(d) List* (SWRCB 2003) to formalize this process and provide the guidelines to be used for listing waters and developing TMDLs, as well as for "de-listing" waters (removing waters from the 303(d) list if the listing was based on faulty data, if objectives or standards have been revised and the segment or water body meets the new standards, or if the standards have been fully attained).

2.3 Basis for the 303(d) Impairment Listing for Selenium

2.3.1 Elevated Levels of Selenium Observed in San Francisco Bay Diving Ducks

Based upon early studies with domestic livestock and poultry, it has long been recognized that excessive accumulation of selenium can cause adverse effects in animals. However, it was not until US Fish & Wildlife Service (USFWS) studies of the accumulation and effects of selenium on aquatic birds nesting around the agricultural drainwater ponds at the Kesterson National Wildlife Refuge began reporting severe reproductive impairment (Ohlendorf et al. 1986; Saiki 1986), including the now infamous pictures of severely deformed embryos and hatchlings, that selenium became a part of the national consciousness. Indeed, the name "Kesterson" has come to assume a similar connotation to that of "Three Mile Island" or "Love Canal".

However, it is important to note that these same investigators had conducted an even earlier study that had already revealed elevated concentrations of selenium in diving ducks (Greater Scaups and Surf Scoters) in San Francisco Bay (Ohlendorf et al. 1986). While the findings of elevated tissue concentrations of selenium in these diving ducks did not receive the same attention as did "Kesterson", they did not go un-noticed.

In response to these findings, the State Board and CA Department of Fish & Game (DFG) conducted a "Selenium Verification Study" from 1985-1990 in which a variety of aquatic organisms from various segments of San Francisco Bay were collected and analyzed for tissue concentrations of selenium (White et al. 1987, 1988, 1989; Urquhart et al. 1991). And indeed, the Selenium Verification Study did "verify" that these diving ducks had elevated tissue concentrations of selenium.

2.3.2 The Initial Basis for Impairment: Health Advisories for Consumption of Waterfowl

Based upon the initial data reported by the Selenium Verification Study (i.e., for the period of January-April 1986), the CA DOHS issued a health advisory for the consumption of tissues from these diving ducks:

> "DHS recommends limiting consumption of scoters to not more than four ounces every two weeks and scaups to not more than four ounces per week. Livers should not be eaten because of high selenium levels. Due to concern on the reproductive and developmental effects of selenium, women of child-bearing age and children 15 of age and under should not eat scoters and scaups from Suisun Bay" (Fan and Book 1986).

Upon review of subsequent data generated by the Selenium Verification Study, the CA DHS issued additional advisories in 1988 (Fan and Lipsett 1988) for San Pablo Bay (Contra Costa, Marin, Solano, and Sonoma counties), and San Francisco Bay (Alameda, Contra Costa, Marin, San Francisco, San Mateo, and Santa Clara counties).

2.3.3 The Initial 303(d) Impairment Listing

In response to the issuance of health advisories for the consumption of the diving ducks by DOHS, the San Francisco Bay Regional Board identified 6 San Francisco Bay segments or water bodies (Table 1; Figure 2) as being impaired due to selenium in 1998:

> "Affected use is one branch of the food chain; most sensitive indicator is hatchability in nesting diving birds, significant contributions from oil refineries (control program in place) and agriculture (carried downstream by rivers); exotic species may have made food chain more susceptible to accumulation of selenium; health consumption advisory in effect for scaup and scoter (diving ducks); low TMDL priority because Individual Control Strategy in place." (SFBRWQCB 1998).

The health advisories against the consumption of diving ducks represent a clear impairment of the beneficial use of commercial and sport fishing: "*Uses of water for commercial or recreational collection of fish, shellfish, <u>or other organisms</u> in oceans, bays, and estuaries, including, but not limited to, uses involving organisms intended for human consumption or bait purposes*" (Table 2).

Table 2. Beneficial uses of San Francisco Bay that are impaired.		
Use	**Abbreviation**	**Definition**
Ocean, commercial, and sport fishing	COMM	Uses of waters for commercial or recreational collection of fish, shellfish, or other organisms in oceans, bays, and estuaries, including but not limited to, uses involving organisms intended for human consumption.

2.3.3.1 Additional Impairment Considerations: Amending the 303(d) List – In 1989, California Water Code was amended to establish a comprehensive program to protect the existing and future beneficial uses of California's enclosed bays and estuaries. The resultant Bay Protection and Toxics Cleanup Program (BPTCP) has four primary goals:

1. protect existing and future beneficial uses of bay and estuarine waters;
2. identify and characterize toxic hot spots;
3. plan for the prevention and control of further pollution at toxic hot spots; and
4. develop plans for remedial actions of existing toxic hot spots and prevent the creation of new toxic hot spots.

As part of the BPTCP, intensive monitoring of numerous sites throughout San Francisco Bay was performed, which led to the identification of several sites as being contaminated with a wide variety of chemicals and trace elements, including selenium (Hunt et al. 1998).

In 2002, the State Board amended the 303(d) list to include those BPTCP sites having elevated chemicals in sediments *and* adverse biological impact as indicated by either sediment toxicity *or* degradation of the benthic community (Table 3; Figure 2).

Table 3. BPTCP Category IV sites[a]: stations with elevated chemistry and biological impact measured by either toxicity or degraded benthos.		
Impaired Water Body	Indicator of Impairment	Linkage of Impairment to Se[b]
Castro Cove	Sediment toxicity to amphipods	Se concentration exceeds the BPTCP 90th percentile value
Central Basin	Sediment toxicity to amphipods (high sulfide); sediment porewater toxicity to urchins (ammonia high)	not identified
San Leandro Bay	Sediment toxicity to amphipods	Se concentration exceeds the BPTCP 90th percentile value
Oakland Inner Harbor (Pacific Drydock Yard 1)	Sediment toxicity to amphipods	not identified
Oakland Inner Harbor (Oakland-Fruitvale)	Sediment toxicity to amphipods (high ammonia, sulfide)	not identified

a - From Table 28 in Hunt et al. (1998).
b – From Table 16 in Hunt et al. (1998).
Note - the San Francisco Bay Regional Board has, in comments to the State Board, expressed concern that the BPTCP had not established a causal link between any adverse effects and any of the elevated contaminant concentrations (SFBRWQC 2001).

If the observed sediment toxicity at these BPTCP sites is, in fact, due to selenium, then we must conclude that several of the Bay's beneficial uses, in addition to the previously mentioned commercial and sport fishing, are being impaired due to elevated selenium (Table 4).

Table 4. Beneficial uses of San Francisco Bay that could potentially be impaired from ambient water toxicity due to selenium.

Use	Abbreviation	Definition
Cold freshwater habitat	COLD	Uses of waters that support cold water ecosystems, including preservation or enhancement of aquatic habitats, plants, fish, or wildlife, including invertebrates.
Ocean, commercial, and sport fishing	COMM	Uses of waters for commercial or recreational collection of fish, shellfish, or other organisms in oceans, bays, and estuaries, including but not limited to, uses involving organisms intended for human consumption.
Estuarine habitat	EST	Uses of waters that support estuarine ecosystems, including, but not limited to, preservation or enhancement of estuarine habitats, vegetation, fish, shellfish, or wildlife (*e.g.*, estuarine mammals, waterfowl, shorebirds), and the propagation, sustenance, and migration of estuarine organisms.
Marine habitat	MAR	Uses of waters that support marine ecosystems, including preservation or enhancement of marine habitats, plants, fish, shellfish, or wildlife.
Fish migration	MIGR	Uses of waters that support habitats necessary for migration, acclimatization between fresh water and salt water, and protection of aquatic organisms that are temporary inhabitants of waters within the region.
Preservation of rare and endangered species	RARE	Uses of waters that support habitats necessary for the survival and successful maintenance of plant of animal species established under state and/or federal law as rare, threatened, or endangered.
Fish spawning	SPWN	Uses of waters that support high quality aquatic habitats suitable for reproduction and early development of fish.
Warm freshwater habitat	WARM	Uses of waters that support warm water ecosystems, including preservation of enhancement of aquatic habitats, plants, fish, or wildlife, including invertebrates.
Wildlife habitat	WILD	Uses of waters that support wildlife habitats, including, but not limited to, the preservation and enhancement of vegetation and prey species used by wildlife, such as waterfowl.

2.3.4 Consistency of the 303(d) Listing with Current State Policy

Although the listings of Bay segments as impaired by selenium occurred prior to the issuance of the State Board's formal 303(d) listing policy, they are consistent with current state policy that water segments shall be placed on the section 303(d) list if any of the following conditions are met:

1. exceedance of numeric water quality objectives for toxic pollutants (e.g., California/National Toxics Rule water quality criteria);
2. exceedance of numeric water quality objectives for conventional pollutants;

3. exceedance of bacteria water quality standards;
4. **issuance of a health advisory against consumption of edible resident organisms, or issuance of a shellfish harvesting ban;**
5. tissue contaminant concentrations in resident organisms that exceed a pollutant-specific evaluation guideline;
6. **exhibition of statistically significant water or sediment toxicity;**
7. exceedance of a nutrient-related evaluation guideline that is associated with "nuisance" excessive algal growth, unnatural foam, odor or taste;
8. exceedance of any other acceptable (non-nutrient) evaluation guideline for "nuisance" taste, color, oil sheen, turbidity, litter, trash, and odor;
9. exhibition of adverse biological responses in resident organisms relative to reference conditions;
10. exhibition of any significant degradation of biological populations or communities relative to reference conditions;
11. exhibition of any *trend* of declining water quality (SWRCB 2003).

3. A Conceptual Model for Selenium

The conceptual model of the fate and effects of selenium in the San Francisco Estuary watershed integrates information on the sources and loading of selenium to the Bay, the chemical characteristics of selenium, and the linkages between these and the resultant cycling and bioaccumulation of selenium. Because selenium can and does occur in a wide variety of different chemical forms, a normal discussion of "cycling" processes can rapidly become overly complex. As a result, the formal discussion of cycling processes in this CMIA is limited to those involved in selenium bioaccumulation; other cycling processes may be discussed in other sections of this conceptual model, as appropriate.

3.1 Selenium: Background Information

Like mercury, selenium is a natural trace element (number 34 on the periodic table (Figure 3), directly below sulfur). That is, it occurs naturally in the environment, unlike PCBs, legacy pesticides, and many of the other contaminants that occur in San Francisco Bay. And like mercury, many of the problems that selenium can cause in aquatic ecosystems result from:

1. mobilization of selenium from terrestrial sources into surface waters,
2. transformation of inorganic forms into organic forms, and
3. bioaccumulation of these organic forms into higher trophic level organisms.

An understanding of these key processes is an essential first step towards understanding what happens to selenium in San Francisco Bay and determination of whether or not selenium is currently impairing the Bay's resources and beneficial uses.

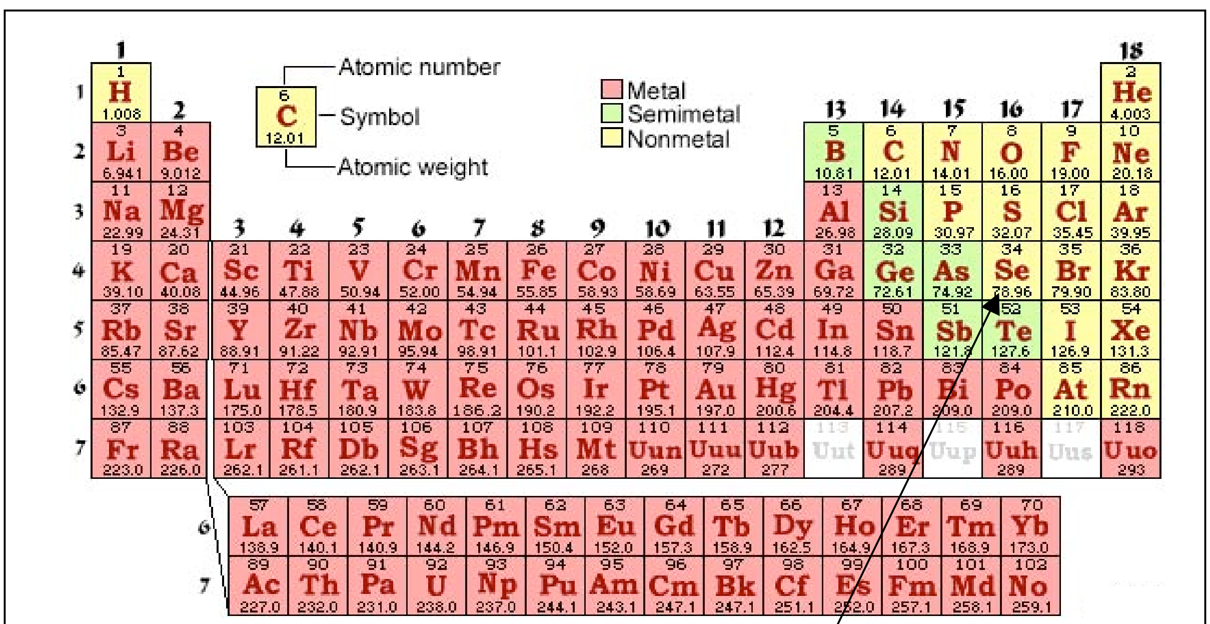


Figure 3. The Periodic Table of Elements. Note that selenium, atomic number 34, lies directly below sulfur; the chemical similarity between these elements that is indicated by their relative positioning is key to the fate and effects of selenium.

Selenium occurs in several different chemical forms or *species* (Table 5). Due to its chemical similarity to sulfur, these selenium species are typically direct analogs to similar sulfur species. In most oxic waters, selenium will be most stable in its most oxidized form, Se^{+6}, which typically occurs as the oxyanion **selenate** (SeO_4^{+2}), a direct analog to sulfate (SO_4^{+2}). The uptake and biotransformation of selenate into organoselenides by the microbes and algae at the base of the food chain is greatly reduced relative to selenite (see review by Ogle et al. 1988), and these processes are further inhibited by sulfate (Williams et al. 1994; US EPA 2004). Selenate behaves as a non-sorbing solute, and relative to selenite, is much less likely to adsorb to particulates and become incorporated into sediments (Zhang and Moore 1997; Guo et al. 1999). As the amount of available oxygen in water decreases, the preferred stability to selenium shifts towards a slightly more reduced form, Se^{+4}, which typically occurs as the oxyanion **selenite** (SeO_3^{+2}), a direct analog to sulfite (SO_3^{+2}). In contrast to selenate, selenite is readily taken up by the microbes and algae at the base of the food chain, and is rapidly biotransformed into organoselenides, such as seleno-amino acids (see review by Ogle et al. 1988). Selenite also readily sorbs to particulate material, particularly Fe/Mn oxides (Neal et al. 1987; Balistrieri and Chao 1990).

Loadings of selenate and selenite can both push adsorption and phytoplankton uptake towards higher particulate selenium concentrations, it's just that selenite pushes harder, pound for pound. The approximately 10-fold difference in the bioavailability of selenite relative to selenate led Regional Board staff to propose a 10:1 ratio for managing selenium loads (Taylor, 1997). In the environment, selenium will shift back and forth between these forms depending upon the ambient water quality conditions, although in the case of oxidation of selenite to selenate, the reaction rate may be exceedingly slow, i.e., on the order of 10^3 years (Cutter and Bruland 1984).

As the amount of available oxygen in water continues to decrease, as might be common in sediment interstitial waters, the preferred stability to selenium again shifts towards a more reduced form, Se^0, or **elemental selenium**. Elemental selenium is insoluble, and occurs in particulate form. The formation of elemental selenium from the more oxidized forms can be facilitated by anoxic microbes in a process termed "dissimilatory reduction" (Zehr and Oremland 1987; Steinberg and Oremland 1990).

Under extremely reducing conditions, selenium may be reduced further to form **selenide(s)**, Se^{-2}. Like inorganic sulfides, **inorganic selenide** can bind very strongly to metal ions, forming insoluble precipitates. However, an even more important pathway for the conversion of selenium to the Se^{-2} form is *biotransformation*, in which living cells absorb one of the more oxidized forms of selenium, and then reduce the selenium biologically and incorporate it into a wide variety of organic compounds, such as seleno-amino acids (e.g., selenomethionine); the resultant **organoselenides** (which are often referred to as "particulate" selenium) are then available, both in living cells and in detrital materials, for bioaccumulation by consumer organisms. Selenium can also occur as *methylated* selenides which are volatile and serve as a means of selenium loss from water and sediments to the atmosphere.

Table 5. Chemistry and significance of selenium species in natural waters.			
Oxidation State	Selenium Species	Key Characteristics	Importance to Selenium Cycling
Se^{+6}	Selenate (SeO_4^{+2})	Extremely soluble with a very low affinity for sorption to particulates. Thermodynamically most stable in oxic waters.	Principal form in minerals (e.g., marine shales), therefore dominant species in leached agricultural drainwaters. Very low bioaccumulation and/or biotransformation by algae. Uptake is inhibited by sulfate.
Se^{+4}	Selenite (SeO_3^{+2})	Extremely soluble with a much greater affinity for sorption to particulates than selenate. Thermodynamically less stable in oxic waters, but still common due to very slow oxidation rate.	Principal form of concern as it accumulates in phytoplankton ~10-fold more readily than selenate; Uptake is not inhibited by sulfate.
Se^{0}	Elemental Selenium	Insoluble precipitate, formed primarily from dissimilatory reduction of selenite in anoxic sediments.	Removal pathway from waterbodies; conversion to particulate organoselenium is important bioaccumulation pathway for benthic invertebrates.
Se^{-2}	Inorganic selenide (Se^{2-})	Highly reactive, forms insoluble precipitates with metals analogous to sulfide; Se^{2-} often co-occurs with inorganic sulfide ores (e.g., cinnabar)	Formation of highly insoluble HgSe (cinnabar analogue) may explain mechanism of Hg detoxification by Se.
	Cellular (aka, particulate) Organoselenium	Selenium that has been incorporated into phytoplankton/higher organisms. Selenium substitutes for sulfur in amino acids (e.g. selenomethionine)	Particulate organoselenium is major bioaccumulation pathway for benthic invertebrates (particularly for bivalves like *Potamocorbula*)
	Dissolved Organoselenium (aka, organoselenide)	Dissolved organic compounds (e.g. selenomethionine) released from decaying cellular tissues.	Regenerative pool of selenium with uncertain bioavailability?
	Dimethylselenide, dimethydiselenide	Methylated selenium is produced by microbes, plants, and animals.	Provides gaseous escape from sediments and surface waters into the atmosphere.

3.2 Sources and Loading

The three major sources of selenium to the Bay are:

1. the Sacramento River,
2. the San Joaquin River, which includes seleniferous agricultural drainwater,
3. discharges from oil refineries,

all of which bring selenium into the northern reach of the Bay system (Figure 4). As described earlier, the southern reach of the Bay does not have similar tributary or industrial discharge sources, and acts much more like a tidal lagoon; POTWs are the major sources of selenium to South Bay (Cutter 1989; Cutter and San Diego-McGlone 1990).

3.2.1 Riverine Input of Dissolved Selenium to Northern San Francisco Bay

The **Sacramento River** is the largest source of surface water runoff into San Francisco Bay (Figure 1), with a flow rate that is over 10-times that of the San Joaquin River (Ball and Arthur 1979). Cutter and Cutter (2004) recently reported that the concentrations of total dissolved selenium in the Sacramento River water have been remarkably consistent over time, with values in 1997-99 (Table 6) being essentially identical to those observed in the 1980s; furthermore, the relative proportions of the various selenium species have been similarly consistent: predominantly selenate (48% of the total), with much less selenite (12% of the total), and the remainder being assumed to be dissolved organoselenides (Table 6).

The **San Joaquin River** drains approximately 13,500 mi^2 (Figure 1), much of which is agricultural. Soils on the west side of the San Joaquin Valley are derived from marine geological deposits that are high in selenium and salts, and irrigation and drainage of these saline soils dissolves the selenium (most of which is in selenate form) into the agricultural drainwater, much of which is eventually conveyed to the San Joaquin River (Presser and Barnes 1984; Tanji et al. 1986). As a result, the concentrations of total dissolved selenium in the San Joaquin River are much higher than in the Sacramento River, although recent changes in management practices by agricultural (ag) drainwater stakeholders appear to have been effective in reducing the San Joaquin River water total dissolved Se concentrations in 1997-2000 to less than half that observed in 1984-1988 (Cutter and Cutter 2004). Nevertheless, the selenium concentrations in the San Joaquin River remain elevated relative to the Sacramento River, again being predominantly selenate (66% of the total) with much less selenite (3% of the total), and the remainder being assumed to be dissolved organoselenides (Table 6). However, because of the historical diversion of San Joaquin River water for domestic and agricultural uses prior to discharge into the Delta or northern San Francisco Bay (Arthur and Ball 1979), the contribution of the San Joaquin River as a source of selenium has often been considered negligible (Cutter and Diego-McGlone 1990). This may well change as state-mandated increases in the flow of San Joaquin River water to the Delta and Bay come into play (as per the 1994 Bay-Delta Water Accord, SWRCB 1994).

3.2.2 Mid-Estuarine Sources of Dissolved Selenium: the Oil Refineries

Like sulfur, selenium is a natural constituent of oil, and due to high water solubilities, many of the selenium compounds present in the oil will partition into the wastewater stream. As a result, oil refineries can discharge a variety of selenium species, including selenate and selenite. Studies in the 1980's had identified refinery discharges as being a major source of selenite to the Bay.

Figure 4. A conceptual model of the major sources of selenium into San Francisco Bay.

(Cutter 1989; Cutter and San Diego-McGlone 1990). The San Francisco Bay Regional Board responded with a Mass Emissions Reduction Strategy that required the oil refineries to reduce their loads of selenium to the Bay (SFBRWQCB 1992). The refineries have been extremely successful in achieving these reductions, with the most recent studies indicating an average 66% reduction in total dissolved selenium discharge (Cutter and Cutter 2004), and a remarkable 92% average reduction in the amount of selenite being released (Figure 5).

As reported by Cutter and Cutter (2004), this has resulted in a concomitant change in the Bay's selenium profile: "selenite concentrations, particularly in the Suisun Bay-Carquinez Strait-San Pablo Bay region, have decreased by 82%, roughly that same decrease as that in the refinery effluents…". Cutter and Cutter (2004) concluded, "the present day refinery fluxes seldom exceed the riverine inputs, are largely selenate, and the few data presented here suggest that the refinery inputs have decreased even further

Table 6. Relative concentrations of selenium species (μg/L Se) in the major sources of dissolved selenium into San Francisco Bay.

Selenium Species	Sacramento River[b]	San Joaquin River[c]	Refinery Effluents[d]
Total Se	0.074	0.679	16.34
Selenate	~0.036 (48% of total)	~0.448 (66% of total)	~9.97 (61% of total)
Selenite	~0.009 (12% of total)	~0.020 (3% of total)	~2.29 (14% of total)
organic selenides[a]	~0.030 (40% of total)	~0.210 (31% of total)	~4.09 (25% of total)

a – Calculated as the difference between Total Se and (selenite + selenate).
b – from November 1997 to May 2000 (Meseck 2002).
c – from November 1997 to April 2000 (Meseck 2002).
d – from October 1999 to August 2000 (Cutter and Cutter 2004).

3.2.3 South Bay: The POTWs

Based upon analysis of South Bay ambient waters and POTW effluents, Cutter (1989) concluded that "..the source of selenium (to South Bay) appears to be the effluents from municipal and industrial discharges rather than *in situ* production". This was also supported by follow-up monitoring indicating that the maximum potential selenium loading from the Coyote Creek system was only 10% of that from the municipal sources (Cutter and San Diego-McGlone 1990).

3.2.4 South Bay: The Alviso Slough Puzzle

Selenium concentrations in water at Alviso Slough exceed the California Toxics Rule (CTR)-established chronic water quality objective of 5 µg/L (Figure 6). Because of the concentration gradient leading up to Alviso Slough, and the fact that a temporally intensive study conducted by the City of San Jose (Watson et al., 1998) showed that low-tide selenium concentrations in Alviso Slough are substantially higher than high-tide concentrations, it was initially concluded that the Guadalupe River (which drains into Alviso Slough) was the source of high-selenium waters (Zawislanski, 2003). That report went on to speculate that the source could be geologic disturbances related to the New Almaden mercury mine, presumably due to the association of selenium with sulfide ores.

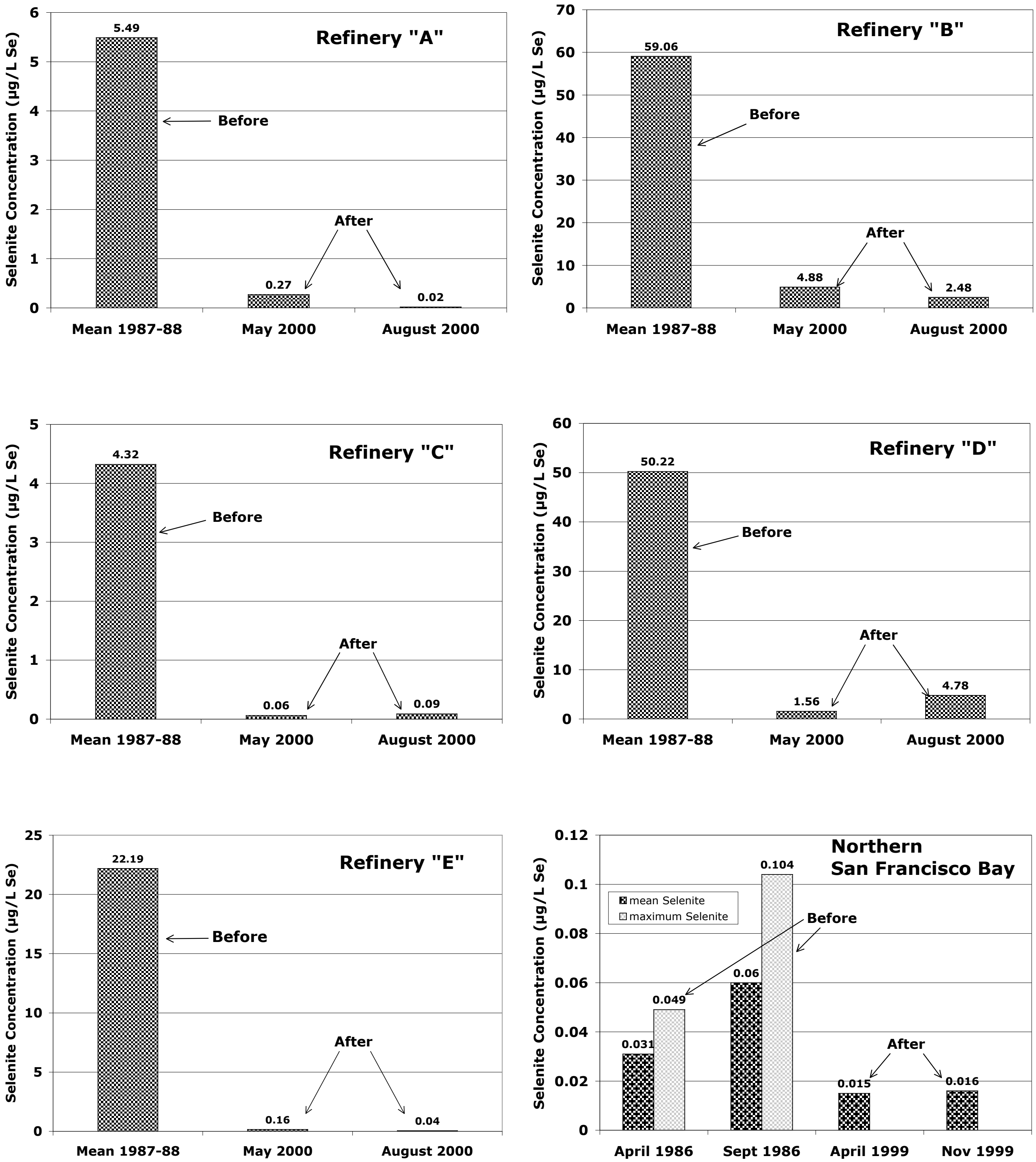


Figure 5. Changes in the selenite levels in the Bay area refinery effluents "before" and "after" refinery-implemented selenium control strategies, and the resultant changes in

northern San Francisco Bay ambient water selenite levels. Data from: Cutter (1989); Cutter and Cutter (2004).

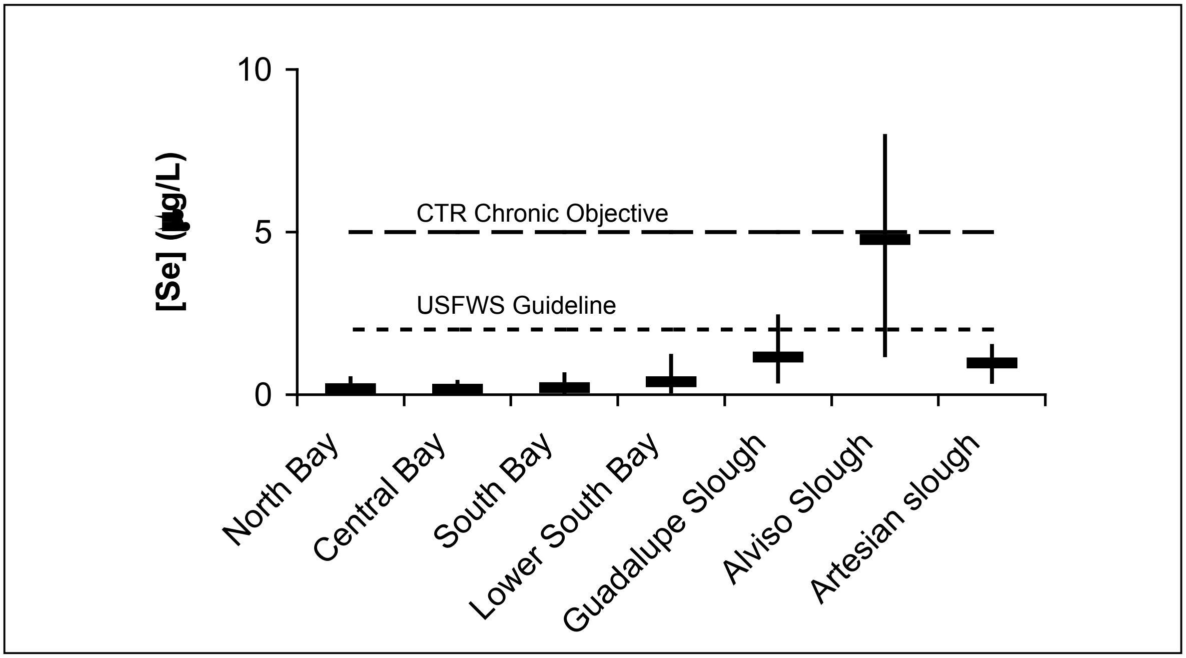


Figure 6. The California Toxics Rule water quality objective for protection against chronic toxicity for selenium (5 µg/L) is frequently exceeded at Alviso Slough. Symbols indicate average and range observed in the RMP.

The tidal variation of selenium in Alviso Slough observed by (Zawislanski, 2003) is an important insight. However, inspection of the relationship between the volume of flow in the Guadalupe River and the selenium concentration at Alviso Slough reveals that mobilization from the upper watershed is not the likely source of high selenium water. When the Guadalupe River is discharging enough water to fill Alviso Slough, the selenium concentration drops to 1-2 ppb. This pattern observed in the RMP data set is confirmed by analysis of the long-term monitoring data produced by the City of San Jose [see, for example, Figure 7 in Zawislanski (2003)].

A more likely explanation is the discharge of pumped groundwater from dewatering operations in the lower Guadalupe River. Selenium concentrations are elevated (2-8 μg/L) in groundwater wells in the alluvial plain between Coyote Creek and the Guadalupe River (Santa Clara Valley Water District, 1994), so groundwater dewatering operations that involve substantial volumes may need to be investigated as potential selenium sources.

3.2.5 Sources of Suspended Particulate Selenium

Unlike microbes and algae, the primary source for selenium bioaccumulation by consumer organisms is via the food chain. At the lower trophic levels, this will consist primarily of ingestion of particulate materials (i.e., microbes, algae, detritus, as well as abiotic particulate materials). Recent studies have revealed that, on average, suspended particulate material in San Francisco Bay comprises 5-12% of the total amount of selenium in the water column (although it can range from 2 to 18%, depending upon location), the remainder being the dissolved selenium species discussed previously (Doblin et al. 2005).

Particulate selenium can be found in any of its oxidation states:

1. organic selenides (e.g., cellular selenium, such as bacteria and algae),
2. elemental selenium, or
3. adsorbed or co-precipitated selenite of selenate.

Organic selenium comprises a large part of the particulate fraction (averaging ~45% of the total), with varying amounts of elemental selenium and adsorbed selenite(+selenate); however, under high flow conditions, the elemental selenium fraction increases. Because elemental selenium is generally only formed in anoxic sediments, it can be concluded that resuspended sediments are the source of a large amount of the suspended particulates, and that contribution can be estimated based on the observation that Bay-Delta sediments average 53-57% elemental selenium (Doblin et al. 2005). Using this approach, Doblin et al. (2005) concluded that resuspension of sediment contributes an average of 83% (ranging from 35% to 100%) of the suspended particulates, with the remainder assumed to be cellular (microbial and algal) organoselenides. This was reiterated in Meseck's (2002) conclusion that while dissolved selenium in San Francisco Bay is largely controlled by riverine and oil refinery inputs, particulate selenium is a function of riverine inputs of sediment and phytoplankton productivity.

The largest source of suspended particulate material to northern San Francisco Bay is resuspension of riverine and Delta sediments. Over the past 150+ years, human activities, including historical mining activities and more recent agricultural activities, have resulted in a significant amount of particulate material to have settled or become deposited in the Delta. Today, these materials can be re-suspended and conveyed through northern San Francisco Bay. Stormwater runoff events are arguably the greatest cause of re-suspension of sediments (hence Doblin et al.'s (2005) observation of elevated proportions of elemental selenium in the suspended particulate material during high flows), although there are many other factors that affect the transport of suspended sediments from the Delta into San Francisco Bay, including human activities, tides, wind, and water diversions.

3.2.6 Sediment-Water Interchange of Selenium

Recent studies using stable isotope ratios to discern sources of selenium to northern San Francisco Bay sediments concluded that the reduction of selenium from the overlying water is not a significant mechanism for incorporation of selenium into the sediments (Johnson et al. 2000). This is consistent with recent sediment and sediment porewater studies that indicate that while there is a very small flux of inorganic selenium into sediments and a very small flux of organic selenium out of sediments, the net flux of total selenium between the water column and sediments is relatively negligible (Meseck 2002).

3.2.7 Volatilization of Selenium From San Francisco Bay

Under appropriate conditions, microbes (bacteria and fungi), algae and plants can form dimethylselenide and dimethyldiselenide which can be volatilized and released to the atmosphere (Ansede and Yoch 1997). Dimethylselenide loss to the atmosphere was estimated to be 10-30% of the selenium removal pathway in a treatment wetland from a Bay Area refinery (Hansen et al., 1998). In the Gironde Estuary (France), methylation was estimated to result in the flux of 60-260 kg/yr of selenium out of the estuary (Amoroux and Donard 1997).

3.2.8 Estimation of Selenium Loading into San Francisco Bay
Based upon the above characterization of the movement of dissolved selenium into and out of the sediments (Section 3.2.6), and consistent with Cutter and Cutter's (2004) estimates of internal fluxes of selenium with the Bay, transfer between water and sediments is ignored in this initial analysis.

3.2.8.1 Riverine Fluxes via the Delta – The loading of dissolved selenium from the Central Valley was calculated by taking the concentrations measured at the Sacramento River and San Joaquin River monitoring stations, weighting them proportionate to their Delta outflow contributions, and then computing a "river end member concentration", which is then multiplied by the net freshwater discharge from the Delta (= the DWR's "Net Delta Outflow Index [NDOI]), as described in Cutter and Cutter (2004).

Selenium loading via particulates from the Delta was calculated by multiplying the particulate selenium concentrations reported by Doblin et al. (2005) by the riverine discharge rates from the Delta (Cutter and Cutter 2004).

There is a great deal of uncertainty in the future loads from the San Joaquin River because the disposal alternatives for agricultural drainwater from the San Joaquin Valley have not yet been resolved. If in-valley or ocean disposal is selected by the United States Bureau of Reclamation (USBR), then the future load from agriculture could become negligible. If Delta-disposal is selected, then the future loading could increase dramatically. An important qualifier in the mass load estimates for the riverine fluxes of selenium from the Delta (and potentially important management question) are the diversions into the California Aqueduct, recycling into the Delta Mendota Canal and other water appropriations and diversions. Another key uncertainty is the timing and location of discharges compared to diversions: freshwater flow is diverted to southern California during the wet season and draws primarily Sacramento River water; this tends to increase the wet season impact of San Joaquin River discharges on the water quality of the Delta.

3.2.8.2 Oil Refinery Effluent Discharges - Selenium loads from refinery effluent discharges were calculated by multiplying the effluent selenium concentrations reported by Cutter and Cutter (2004) by the effluent discharge rates reported by Cutter and Cutter (2004) and by the individual refineries. It may be important to note that the refinery loading rates decreased significantly over the course of Cutter and Cutter's (2004) study, from 552 to 204 kg Se/year; Cutter and Cutter (2004) interpreted this trend as suggestive that "refinery inputs have decreased even further".

3.2.8.3 Municipal Wastewater, Local Tributaries, and Urban Runoff - The assumption that municipal wastewater, local tributaries, and urban runoff are likely minor selenium sources is supported by their discharge volumes and selenium concentrations and some simple calculations. The average annual runoff volume (urban and non-urban) for the Bay Area is about 900 million cubic meters (McKee et al., 2002). Annual effluent discharge volumes are similar to this, about 866 million cubic meters (Grovhoug et al., 2004). If the flow-weighted average selenium concentration is 0.1 μg/L in a discharge volume of 900 million cubic meters, the selenium load would be 90 kg, a minor source compared to the riverine fluxes shown in Table 7. However, if the flow-weighted average concentration is 1 μg/L, the annual load for the same discharge volume would be 900 kg, a load comparable load to the other sources shown in Table 7.

Accurate selenium concentration data for local tributaries and wastewater are sparse – typical detection limits are around 1 μg/L, and data are often "non-detect". Wastewater selenium concentrations are largely a function of the selenium concentration in municipal drinking water sources (Santa Clara Valley Water District 1994). Given what is known about selenium concentrations in typical surface waters (e.g., the Sacramento River [see Table 6]), average concentrations in both runoff and effluent are more likely to be closer to 0.1 μg/L than 1 μg/L, but this is an uncertainty that leads to a management question: Are selenium concentrations in Bay Area municipal water supply, effluent, urban, and non-urban streams closer to 0.1 μg/L or 1.0 μg/L? This question is probably more relevant on local scales than Baywide.

Table 7. Selenium loading (kg/yr) to San Francisco Bay.

Source	Sample Collection Period	Range of Loading Rates (kg Se/yr)	
		Dissolved Selenium	Particulate Selenium
Riverine Fluxes of Selenium from the Delta	Nov, 1997 – Nov, 1999	282-9570[a]	47-686[b]
Oil Refinery Discharges	Oct, 1999 – Aug, 2000	204-552[c]	nr
Municipal Wastewater, Local Tributaries, and Urban Runoff	See discussion above	90-900 (?)	nr

a - Loading rates calculated using data from Cutter and Cutter (2004).
b - Loading rates calculated using data from Cutter and Cutter (2004) and Doblin et al. (2005).
c - Loading rates calculated using data from Cutter and Cutter (2004) and refinery effluent discharge rates provided by the individual refineries.
nr – not reported.

3.2.9 Initial Mass Inventory Calculations and Observations

Some important conclusions become apparent from considering simple mass inventory and load estimates for selenium. Unlike PCBs and mercury which are found almost exclusively in sediments, selenium has a relatively low, variable partition coefficient (K_d between 100 and 10,000), and about 80% of total selenium in the water column is dissolved. That means it needs to be modeled in two compartments: water and particulates/sediment (Figure 7).

Following established TMDL analysis methods for the Bay (Abu-Saba and Tang, 2000; Davis, 2002; Looker and Johnson, 2003), the water inventory (1,250 kg) is estimated from the volume of the Bay multiplied by the average dissolved selenium concentration as measured in the RMP data set. The sediment selenium inventory (50,000 kg) is estimated as the mass of sediments in the upper 15 cm times the average sediment selenium concentration measured in the RMP data set. Selenium inputs to the dissolved box encompass the range of 'best case' to 'worst case' from the data in Table 7. Particulate selenium again encompasses the range from the 'best case' to 'worst case' from the data in Table 7. Inputs to the mass inventory calculations, references, and assumptions are summarized in Table 8. Outputs and the conceptual approach are summarized in Figure 8.

Table 8. Input terms for selenium mass inventory and residence time calculations

Input	Value	Reference
Volume of the Bay	6.66×10^9 m^3	Conomos (1979)
Mass of active sediments (15 cm depth)	1.4×10^{11} kg	Davis (2002) Looker and Johnson (2003)
[Se] in water	0.187 μg/L	Average of RMP data (1993–present; north of Dumbarton Bridge)
[Se] in Bay sediments	0.36 μg/g	RMP data (1994–present); slope of best fit line with intercept forced to zero (see discussion in Abu-Saba (2003)).
Dissolved selenium load to water column	575-11,000 kg/yr	Range encompassed by the 'best case' to 'worst case' from data in Table 7.
	2500 kg/yr	Nominal average value (from range above) used in mass balance calculations.
Particulate selenium flux from Delta	47-686 kg/yr	Range encompassed by the 'best case' to 'worst case' from data in Table 7.
	<1000 kg/yr	Nominal upper limit value (from range above) used in mass balance calculations.

It is helpful to compare and contrast the mass balance of selenium to that of mercury (Looker and Johnson, 2003). Note that while the Bay's sediment inventories of selenium and mercury are comparable (about 50,000-60,000 kg) because they have similar sediment concentrations, the Bay's water selenium inventory (1250 kg) is ten times that of mercury (140 kg, Looker and Johnson, 2003).

The fact that most of the water column selenium is in the dissolved phase means water selenium inventories can be removed more quickly by flushing. This is reflected in the recent findings that the 90% reduction in refinery loads of selenite was accompanied by a rapid response in the water column concentrations of dissolved selenium (Cutter and Cutter 2004).

However, the sediment selenium inventory in the Bay (and in the upstream riverine and Delta sources) will almost certainly have a longer response time relative to the water inventory. This may be a contributing factor to the observation that while the concentrations of dissolved selenium in the Bay's waters have seen huge declines, there has been no corresponding decline in the suspended particulate matter selenium concentrations (Doblin et al. 2005). Furthermore, as it is primarily the concentration of *suspended particulate selenium* that drives the tissue selenium concentrations of filter feeding bivalves, this linkage explains why there has similarly been no decline in the *P. amurensis* selenium concentrations (Linville et al. 2002; Stewart et al. 2004). As a result, and, depending upon the extent that the *in situ* bedded sediments may contribute to the suspended particulate selenium load, the "active sediment" layer that affects organisms like the clams may be much less than 15 cm. This would indicate a response time shorter than 50 years, though still longer than the water column. In addition, it is interesting to note that the RMP data suggest that there was a “pulse” of elevated selenium in northern San Francisco Bay in September of 1993 (Figure 13), that decreased to intermediate concentrations by February 1994, returning to “normal” levels thereafter (Figure 13), which is mirrored by a similar ‘pulse’ of elevated selenium in the northern San Francisco Bay water column during this same period (Figure 11). This apparent rapid recovery of the northern San Francisco Bay sediment selenium concentrations suggests that the recovery rate for the sediment compartment may be much greater than is predicted by this simple model.

In summary, simple mass balance considerations help understand some general trends in the responses of different indicators to management actions already initiated. To effectively manage selenium, we will have to look at finer scale spatial and temporal trends, and how selenium fate and effects are controlled by speciation and biological transformations.

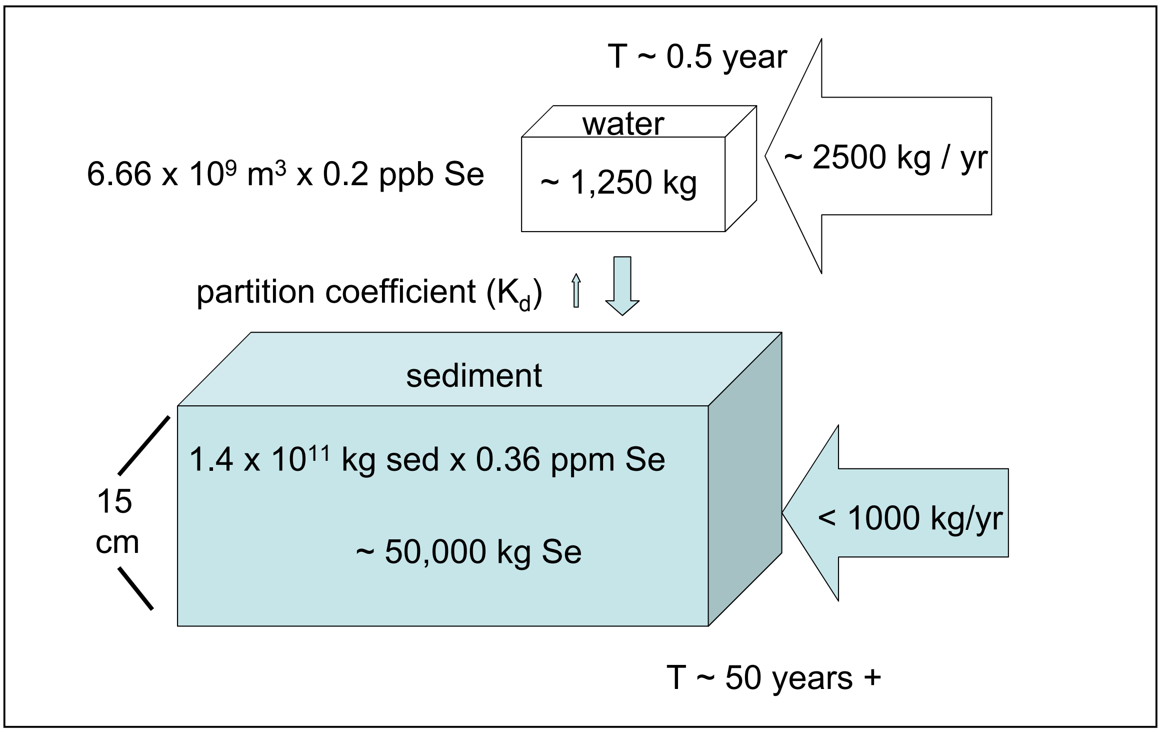


Figure 7. Initial selenium mass balance for the Bay, using a two compartment model for the Bay. The much shorter residence time (T = inventory / input) of selenium in water (0.5 year) compared to sediments (50 years or more) predicts a short response time for water column indicators, but not necessarily for sediment. The sediment mass indicates the mass of sediments in the upper 15 cm of actively resuspended or reworked sediments for the Bay, the water volume indicates volume of the Bay. **Note** that recent studies indicate that the net flux of total selenium between sediments and the water column is relatively negligible (see Table 4 in Meseck 2002), and this interchange is therefore not considered in this two-compartment model.

3.3 Selenium Cycling and Bioaccumulation

While dissolved selenium species can cause direct toxicity to aquatic organisms, the lethal threshold concentrations (e.g., LC_{50} values) are typically much, much higher than the waterborne concentrations seen in all but the most contaminated of ecosystems. This is one reason why historical derivations of water quality criteria using the standard approach of evaluating waterborne toxicity data have arrived at such relatively high values (e.g., the most recent derivation of an acute criterion of selenite in saltwater [US EPA 2004] arrived at a concentration, many orders of magnitude higher than the concentrations measured in the San Francisco Estuary's ambient waters). As a result, the direct toxicity of waterborne selenium will not be addressed in this CM/IA.

However, the reproductive and other health impairments that can result from ***bioaccumulation*** of selenium up through the food chain can be a toxicity issue of 'real world' concern, as evident by the DOHS health advisories and the observation of waterfowl and fish reproductive problems at Kesterson and elsewhere.

Surface waters and effluent discharges that enter the Bay can convey selenium into the Bay's waters in a variety of forms (Figure 8), including:

- Dissolved selenate and selenite,
- Particulate elemental selenium,
- Selenite adsorbed to inorganic or organic particulate material (selenate is much less prone to adsorption),
- Cellular organoselenium, either in living cells or in dead/senescing cells,
- Dissolved organoselenides, typically the exometabolites of algae, but also the compounds that results from the dissolution or release of former cellular material (i.e. cytosolic selenium) from dead/senescing cells.

The sources and loading of selenium into the Bay have been discussed previously. Depending upon the residence time within the Bay's waters, much of the selenium entering the Bay may be flushed out to the ocean without ever being taken up by or even interacting with the Bay's biota. For instance, selenate is much less readily taken up by fungi, bacteria, and algae than is selenite (see below); at times of high flow, it might well be that much (if not most) of the selenate that enters the Bay may pass through to the ocean without ever entering the bioaccumulation process.

3.3.1 The Bioaccumulation and Biotransformation of Dissolved Selenium

Traditional consideration of bioaccumulation, or trophic transfer, begins with the dissolved contaminant being taken up by primary producers (e.g. algae or phytoplankton) as the "base" of the food chain. However, it is important to note that microbial uptake (by fungi and bacteria) can often be just as, or an even more important first step in the eventual bioaccumulation by consumer organisms.

Moreover, it is the bacteria, fungi, and algae that will perform the most critical selenium biotransformation step: the reduction of selenite and selenate and incorporation of the reduced selenides into seleno-amino acids, particularly *selenomethionine*, an analog to the essential amino acid methionine (due to its chemical similarity, the selenium is 'mistakenly' used in place

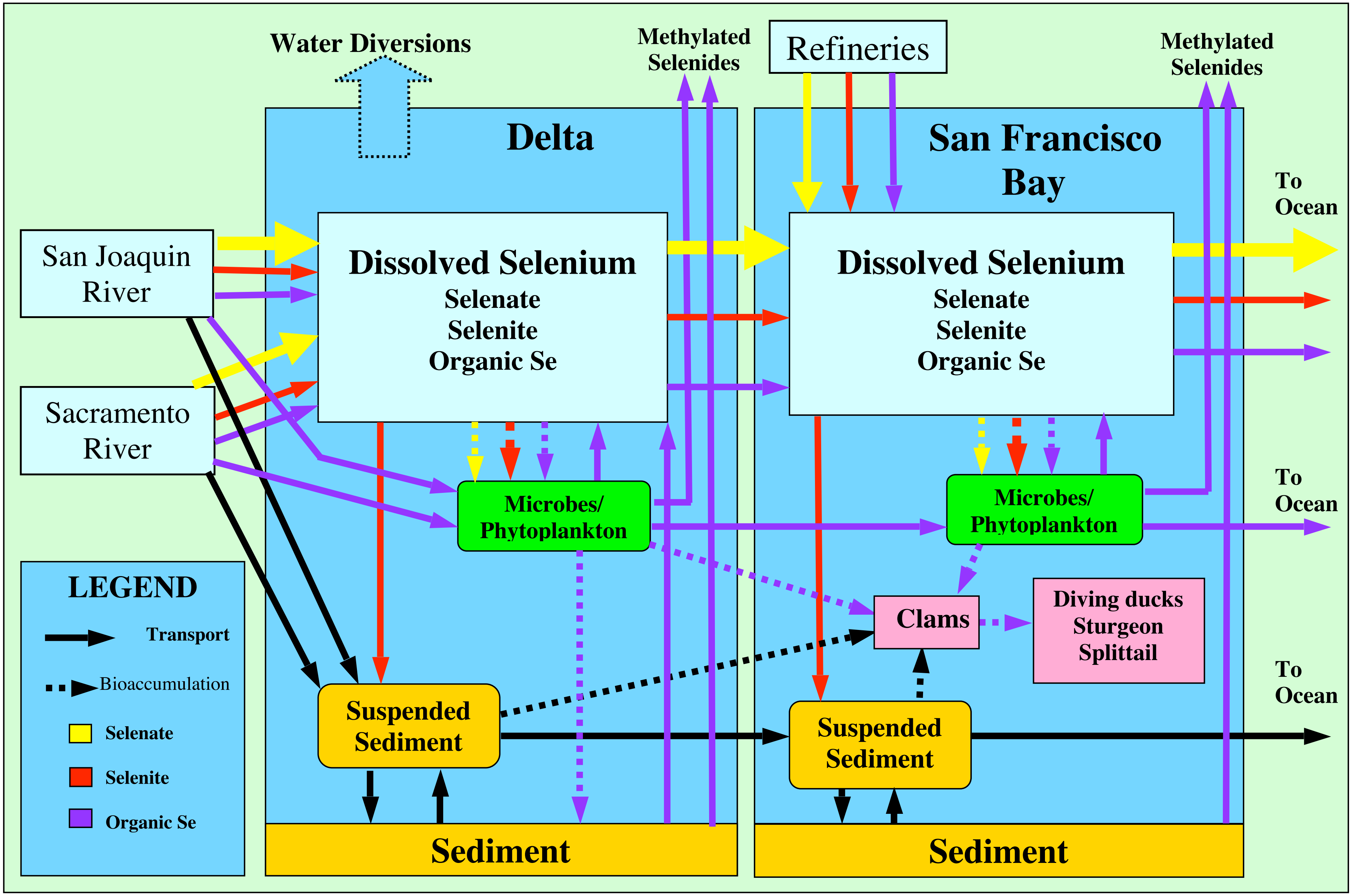


Figure 8. A conceptual model of the transport and bioaccumulation of the key selenium forms and matrices in SF Bay.

of sulfur in the synthesis of this compound). Methionine is an essential amino acid, meaning it cannot be produced by higher-level consumer organisms, who rely upon the synthesis by the lower organisms and subsequent trophic uptake to provide this biologically necessary compound (Robinson et al. 1978; Kim et al. 1992) and who have developed specialized cellular mechanisms to facilitate its uptake and accumulation. Unfortunately, when the presence of selenium results in the mistaken synthesis of selenomethionine, it is the selenomethionine that becomes bioaccumulated by the consumer organisms. And studies have demonstrated that it is this food-borne selenomethionine that is the major cause of much of the observed reproductive problems in fish and waterfowl (Woock et al. 1987; Heinz et al. 1989; Coyle et al. 1993).

3.3.1.1 Microbial Uptake and Transformation of Selenium - Studies have indicated that selenite uptake by **marine bacteria** is rapid with the selenium being biotransformed into seleno-amino acids and proteins within 10 minutes of exposure (Foda et al. 1983), suggesting that bacteria may be an important vector in the bioaccumulation of organoselenides by bivalves, ducks, and fish. Recent studies of the uptake of selenium by intact plankton communities in the Sacramento/San Joaquin River Delta revealed that bacteria accounted for 34-49% of the total selenium uptake (Baines et al. 2004). Furthermore, while selenite was readily taken up by bacteria and incorporated into amino acids and proteins, selenate was not (Foda et al. 1983), suggesting significant differences in the cycling, fate, and effects of selenite vs. selenate.

Estuarine/marine **fungi** are important in organic matter processing and as a food source in detrital particles. Uptake experiments have indicated that while the aquatic fungus *Cryptococcus albidus* was able to take up and reduce selenite, it could not reduce selenate (Brown and Smith 1979), again suggesting that selenate is less able to be reduced and incorporated in organoselenides.

3.3.1.2 Algal Uptake and Transformation of Selenium - There have been a number of studies with a wide variety of algae, which again have indicated that selenite is readily taken up and accumulated whereas the uptake of selenate is much more limited (Wheeler et al. 1982; Wrench and Measures 1982; Lindstrom 1983; Apte et al. 1986; Harrison et al. 1988; Vandermeulen and Foda 1988; Hu et al. 1996). Loadings of selenate and selenite can both push phytoplankton uptake towards higher selenium levels, it's just that selenite pushes harder, pound for pound. The approximately 10-fold difference in the bioavailability of selenite compared to selenate led Water Board staff to propose a 10:1 ratio for managing selenium loads (Taylor 1997).

In a recent study, Baines and Fisher (2001) exposed several marine algal species to seawater amended with 0.15 nM selenite (the approximate concentration reported for ambient water in northern San Francisco Bay [Cutter and Cutter 2004]), and observed that the algal cell concentrations varied by almost 5 orders of magnitude between the species (Table 9), with green algae (as a group) and diatoms exhibiting the lowest concentrations. Although their selenite exposure concentration (90 nM) was markedly higher than the Bay's ambient waters, Doblin et al. (2005) also reported that green algae and diatoms (as algal classes) accumulated the least selenium, much less than dinoflagellates.

Table 9. Cellular selenium concentration (ng/μm^3) for marine algae exposed to 0.15 nM selenite.

Taxonomic Class	Algal Species	Cellular Se Concentration (ng/μm^3)
Bacillariophyceae (diatoms)	*Skeletonema costatum*	4.95×10^{-13}
Chlorophyceae (green algae)	*Chlorella autotrophica*	4.73×10^{-11}
Chlorophyceae (green algae)	*Nannochloris atomus*	5.46×10^{-11}
Chlorophyceae (green algae)	*Dunaliella tertiolecta*	1.21×10^{-10}
Bacillariophyceae (diatoms)	*Chaetoceros gracilis*	3.31×10^{-10}
Bacillariophyceae (diatoms)	*Thalassiosira pseudonana*	1.09×10^{-9}
Dinophyceae (dinoflagellates)	*Prorocentrum minimum*	3.08×10^{-9}
Cryptophyceae (golden brown algae)	*Cryptomonas sp.*	4.90×10^{-9}
Prymnesiophyceae	*Emiliania huxleyi*	3.37×10^{-8}

From: Baines and Fisher (2001).

Furthermore, more detailed studies with the diatom *Thalassiosira pseudonana* indicated a saturation of selenium accumulation in cells at selenite concentrations between 0.1 to 10 nM selenite (Baines and Fisher 2001); similar results were observed for other algal species (except for *Skeletonema*): the selenium concentrations of the algal cells did not vary in proportion to selenite concentrations but remained almost constant over a 30-fold variation in ambient selenite from 0.15 to 4.5 nM, suggesting that the algal tissue concentrations of selenium in San Francisco Bay are less responsive to changes in the Bay's ambient water selenium concentrations than might otherwise have been expected (Baines and Fisher 2001).

Studies with the marine algae *Tetraselmis tetrahele* and *Dunaliella minuta* reported that selenite was readily biotransformed into seleno-amino acids (Wrench 1978); similar results have also been reported for many other marine algal species (Wrench and Campbell 1981; Bottino et al. 1984; Vandermeulen and Foda 1988; Boisson et al. 1995). While much (if not most) of this biotransformed organoselenium is retained within the cellular tissues and eventually ingested by consumer organisms, studies have indicated that live and dead algae will release organoselenides back into the water (Vandermeulen and Foda 1988; Fisher and Wente 1993; Besser et al. 1994; Hu et al. 1996); whether or not these released organoselenides re-enter the food chain is uncertain as there are conflicting reports regarding their apparent bioavailability and uptake (Cutter and Bruland 1984; Cutter and Cutter 1998; Baines et al. 2001).

3.3.2 The Bioaccumulation of Selenium by Invertebrates

It has long been recognized that assimilation of ingested selenium (i.e., from the diet) is the primary mechanism for bioaccumulation of selenium by invertebrates (Fowler and Benayoun 1976; Sanders and Gilmour 1994; Zhang et al. 1990; Luoma et al. 1992; Wang et al. 1996; Ogle 1996; Wang and Fisher 1999).

3.3.2.1 Selenium Bioaccumulation by Zooplankton - Again, traditional analysis of food chain bioaccumulation by invertebrates would focus upon the transfer from phytoplankton to zooplankton. And certainly, zooplankton are a critical component of the Bay's food web. In a study of assimilation efficiency of dietary trace elements by zooplankton, the diatom *Thallasiosira pseudonana* was cultured in radio-labeled selenium and then fed to copepods (Fisher and Reinfelder 1991; Reinfelder and Fisher 1991); it was observed that the assimilation of selenium was 97%, the highest of all the trace elements examined, and that the assimilation was related directly to the amount of selenium in the algal cell cytoplasm. Similar studies feeding *Thalassiosira* to planktonic oyster larvae (*Crassostrea gigas*) observed that none of the diatom's selenium was assimilated, presumably due to the inability of the oyster larvae to open the diatom's silaceous shell (Reinfelder and Fisher 1994); however feeding the alga *Isochrysis galbana* to planktonic oyster and clam larvae resulted in similarly high assimilation efficiencies of 97-100% (Reinfelder and Fisher 1994), again related directly to the amount of selenium in the algal cell cytoplasm.

However, although efficient at assimilating selenium, zooplankton do not appear to accumulate selenium to concentrations much higher than present in their microbial/algal diet (Baines et al. 2002) perhaps due to their relatively high excretion rate of the assimilated selenium (Wang and Fisher 1998; Xu et al. 2001). Recent studies of selenium in San Francisco Bay zooplankton reported that the zooplankton tissue concentrations were generally similar to those found in other "uncontaminated " systems and generally without any spatial trends in the Bay (Purkerson et al. 2003) although the observation of markedly higher concentrations in the Fall of 1999 that coincided with a peak concentration in particulate selenium suggests that zooplankton in the Bay may be subject to occasional increases in selenium content.

3.3.2.2 Selenium Bioaccumulation by Bivalves - Bivalves have been shown to similarly exhibit extremely high assimilation rates for ingested (i.e., "particulate") selenium (Zhang et al. 1990; Luoma et al. 1992; Wang et al. 1995; Reinfelder et al. 1998) with relatively negligible absorption efficiency of dissolved selenium from water (Luoma et al. 1992; Reinfelder et al. 1997; Wang 2001). However, unlike zooplankton, the bivalves have been observed to accumulate the ingested selenium to concentrations markedly higher than present in the microbial/algal diet (Reinfelder et al. 1998), in part due to their high assimilation rates of the cytosolic selenium, but also to their relatively low excretion rates (Reinfelder et al. 1997; Schlekat et al. 2000).

This difference is most dramatic in the Asian clam ***Potamocorbula amurensis***, an exotic species that invaded San Francisco Bay in the mid 1980's and has since become the dominant benthic organism in much of the bay (Carlton et al. 1990); *P. amurensis* accumulates selenium to much higher concentrations (e.g., 6-20 μg/g, dry wt [Linville et al. 2002]) than were observed for bivalves from other uncontaminated estuaries in northern California (1.7-3.1 μg/g [White et al. 1988]) or for the bivalves previously common in these waters (10-11.4 μg/g for *Mytilus edulis* transplanted into the Carquinez Strait [Risebrough et al. 1977] or 3.9-5.2 μg/g for *Macoma balthica* and *Corbicula fluminea* in Suisun Bay up to the mouth of the Carquinez Strait [Johns et al. 1988]).

Interestingly, while the concentrations of total dissolved selenium, and more importantly, of selenite, declined dramatically in the late 1990's (see previous discussion in Sections 3.2.1 and

3.2.2 and Figure 5 [Cutter and Cutter 2004]), there was not a concomitant reduction in the reported *P. amurensis* tissue concentrations (Linville et al. 2002; Stewart et al. 2004) (Figure 9).

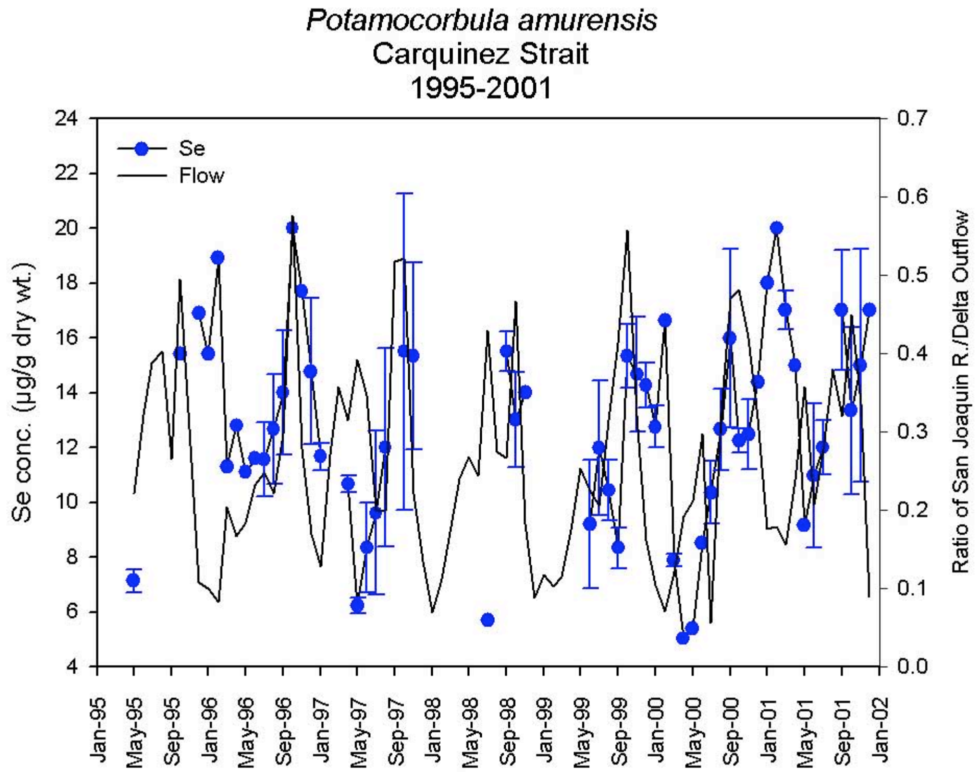


Figure 9. Monthly selenium concentrations (μg/g, dry wt) in *Potamocorbula amurensis* at Carquinez Strait. Also plotted is the ratio of monthly flow from the San Joaquin River relative to total Delta outflow. Data are from Linville et al (2002) and Samuel Luoma USGS (unpublished data). Graph provided courtesy of Robin Stewart, USGS.

This is, in part, due to the fact that selenium uptake from the water is relatively insignificant (Luoma et al. 1992). It is the ingestion and assimilation of particulate selenium that drives bioaccumulation by bivalves, including *P. amurensis* (Luoma et al. 19992; Schlekat et al. 2000, 2002), and in similar contrast with the declining concentrations of selenium in the Bay's water, there has been no decline in the selenium concentrations of the suspended particulate material (Doblin et al. 2005) (Figure 10).

3.3.2.3 The Role of Particulate Selenium in Bivalve Uptake - Suspended particulate selenium is the primary source of selenium bioaccumulated by bivalves like *P. amurensis*. As reported earlier, suspended particulate material (i.e., microbes, algae, detritus, as well as abiotic particulate materials) in San Francisco Bay comprises 5-12% of the total amount of selenium in the water column (Doblin et al. 2005). While only a small part of the particulate material on a mass basis, the microbial and algal biomass have higher selenium concentrations, and as a result, organic selenium is typically the largest fraction of the particulate selenium, ~45% of the total on average. elemental selenium (which can comprise most of the particulate selenium in high flows), and adsorbed selenite(+selenate). Moreover, microbial and algal selenium exhibit extremely high assimilation rates by bivalves (Zhang et al. 1990; Luoma et al. 1992; Wang et al.1995; Reinfelder et al. 1997,1998). Elemental selenium and particle-bound selenite, on the other hand, have much lower assimilation rates (typically <10% [Schlekat et al. 2000]).

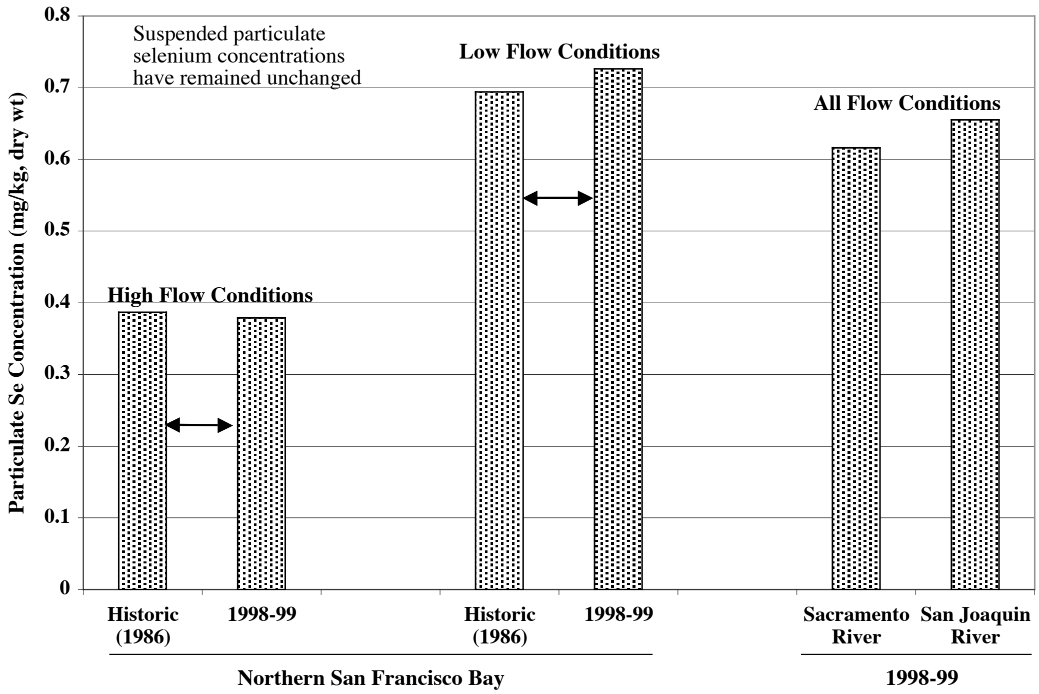


Figure 10. Suspended particulate selenium concentration in northern San Francisco Bay have remained unchanged, despite the significant declines in dissolved selenium concentrations (from Doblin et al. 2004).

Given the number of variables that go into determining suspended particulate selenium levels, it would not necessarily be assumed that there should be a *direct* correlation between dissolved selenium and particulate selenium. However, given the magnitude of the decline in dissolved selenium over the past 20 years, it seems like that there should have been *some* measurable change in particulate selenium … however, none was observed (Figure 10). This, of course. raises the question:

"Why hasn't the selenium concentration of suspended particulates (and the corresponding selenium concentration in the bivalve *P. amurensis*) declined in response to the declines in dissolved selenium in the Bay?"

It has already been indicated that the upstream riverine and Delta sediments are a major source of the suspended particulate selenium. Recent analyses have indicated that the Delta sediment selenium concentrations are actually higher than those in the northern reach of the Bay, and sediment cores in the Delta indicated that the selenium concentrations were generally constant with depth (Meseck 2002). This, combined with the consistency of the dissolved selenium chemistry and speciation in the Sacramento River suggests that the reservoir of upstream sediments provides a steady supply of particulate material to the northern reach of San Francisco Bay with consistent concentrations of selenium that will be independent of the Bay's dissolved selenium concentrations, and therefore, unaffected by the reductions in selenium that were required of the oil refineries.

The absence of any reduction in particulate selenium might also be explained by the selenium uptake of the phytoplankton component. As reported earlier, algal uptake studies have indicated that the algal selenium concentrations did not vary in proportion to selenite concentrations but remained almost constant over a 30-fold variation in ambient selenite, from 0.15 to 4.5 nM (Baines and Fisher 2001). Again, this suggests that algal selenium bioaccumulation is relatively independent of the Bay's dissolved selenium concentrations (at the range of concentrations that have been observed in the Bay), and therefore, unaffected by the reductions in selenium that were required of the oil refineries.

Interestingly, since the introduction of *P. amurensis*, there has been a significant decrease in the amount of phytoplankton in the Bay's waters (Carlton et al. 1990; Alpine and Cloern 1992), which again would suggest that there should have been a proportionate decline in the phytoplankton component of the particulate selenium. However, Lehman (2000) reported that there has also been a significant shift in the phytoplankton community in northern San Francisco Bay with a 60% decrease in diatoms and corresponding increase in green, blue-green, and flagellated algae. As stated above, recent algal uptake studies have indicated that diatoms tend to accumulate less selenium than do other algae (Table 9) (Baines and Fisher 2001; also see Table 22 in Doblin et al. 2004). This suggests that the current phytoplankton fraction of the suspended particulate material will exhibit greater selenium bioaccumulation than before, which could serve to offset the reduction in algal biomass in terms of maintaining consistent particulate selenium concentrations.

3.3.3 Selenium Bioaccumulation by Fish and Waterfowl

Given that the benthic bivalve *Potamocorbula amurensis* tissue selenium concentrations can be so elevated, it is not surprising that the higher trophic level organisms that eat these bivalves will, in turn, exhibit elevated tissue selenium concentrations. In fact, the elevated tissue concentrations of selenium in the Greater Scaup and Surf Scoter that triggered the initial health advisories which led to the current 303(d) listing almost certainly reflect the fact that clams are important food items for these diving duck (Ohlendorf et al. 1986; Fan and Book 1986). Similarly, *P. amurensis* is a dominant food item for white sturgeon and mature Sacramento splittail (Feyrer et al. 2003; Stewart et al. 2004), which are the Bay fish species exhibiting the highest tissue selenium concentrations (Stewart et al. 2004).

In contrast, fish that feed primarily upon the planktonic food chain (i.e., such as juvenile striped bass feeding on zooplankton and other water column organisms) do not exhibit similarly elevated tissue selenium concentrations (Baines et al. 2002; Schlekat et al. 2002; Purkerson et al. 20033; Stewart et al. 2004).

4. Impairment Assessment: Current Conditions

4.1 Compliance with Water/Sediment Quality Objectives

4.1.1 Compliance with Water Quality Objectives

The RMP has monitored water chemistry in San Francisco Bay since 1993. The results of the analyses of selenium in San Francisco Bay ambient waters are summarized in Figures 11 and 12. Numerical water quality objectives for selenium for the protection of aquatic life have been established by the U.S. EPA and the California Toxics Rule (CTR) (Table 10). Examination of the RMP waterborne selenium concentrations reveals that there have been no exceedances of the EPA and CTR criteria; indeed, the ambient concentrations of selenium in the Bay's waters are typically orders of magnitude below the criteria levels.

Table 10. Water quality criteria for selenium

Regulating Agency	Acute Criteria		Chronic Criteria	
	Freshwater	Saltwater	Freshwater	Chronic
U.S. EPA 1987	20 ng/L[a]	300 μg/L[b]	5 ng/L[a]	71 ng/L[b]
U.S. EPA 2004 (draft)	258 μg/L[c] 417 μg/L[d]	127 μg/L[c]	Chronic: Whole-body fish tissue 7.91 μg/g, dry wt	
California Toxics Rule	20 μg/L	290 μg/L	5 μg/L	5 μg/L

a - 1-hr average, not to be exceeded more than once every 3 years.
b - 4-day average, not to be exceeded more than once every 3 years.
c – selenite.
d – selenate; the selenate criterion is mediated by the sulfate concentration (the shown numerical value of 417 μg/L is based upon a sulfate concentration of 100 mg/L).

However, it is difficult to interpret the RMP waterborne selenium data and achieve any meaningful evaluation of impairment. As stated before, the lethal threshold concentrations (i.e. LC_{50} values) are typically much, much higher than the waterborne concentrations seen in all but the most contaminated of ecosystems. This is one reason why historical derivations of water quality criteria using the standard evaluation of waterborne toxicity data have arrived at such relatively high values, many orders of magnitude higher than the concentrations measured in the Bay's ambient waters).

4.1.2 Compliance with Sediment Quality Objectives

There are no existing sediment criteria for selenium, nor any existing sediment quality guidelines such as ERLs and ERMs. US FWS selenium experts have established 4 μg/g, dry wt, as the maximum allowable selenium concentration in their guidance for TMDLs (Lemly 2000). The RMP sediment selenium concentration data indicate that the sediment concentrations in the Bay are typically much lower than this guidance threshold, including the worst-case data observed 1993 (Figure 13).

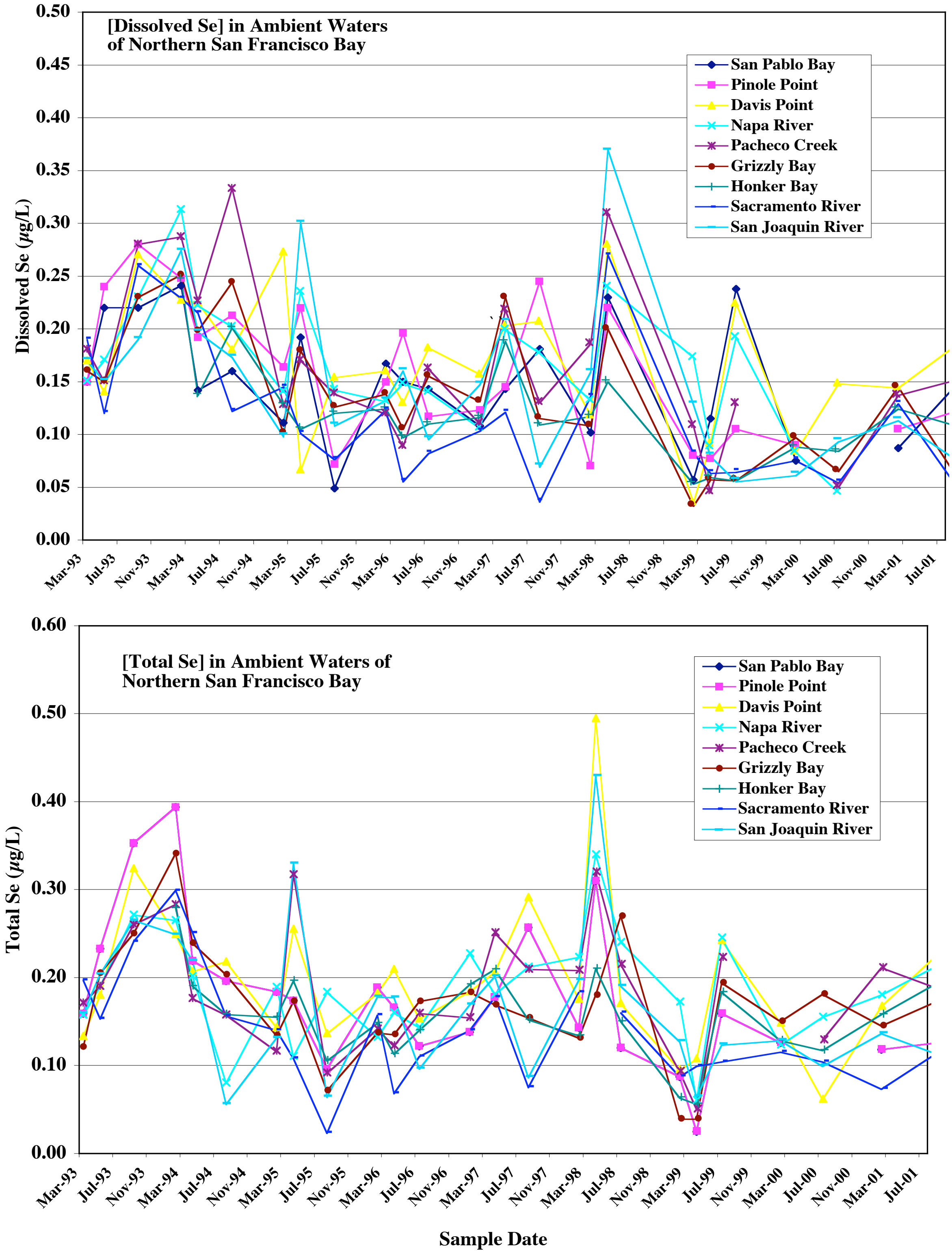
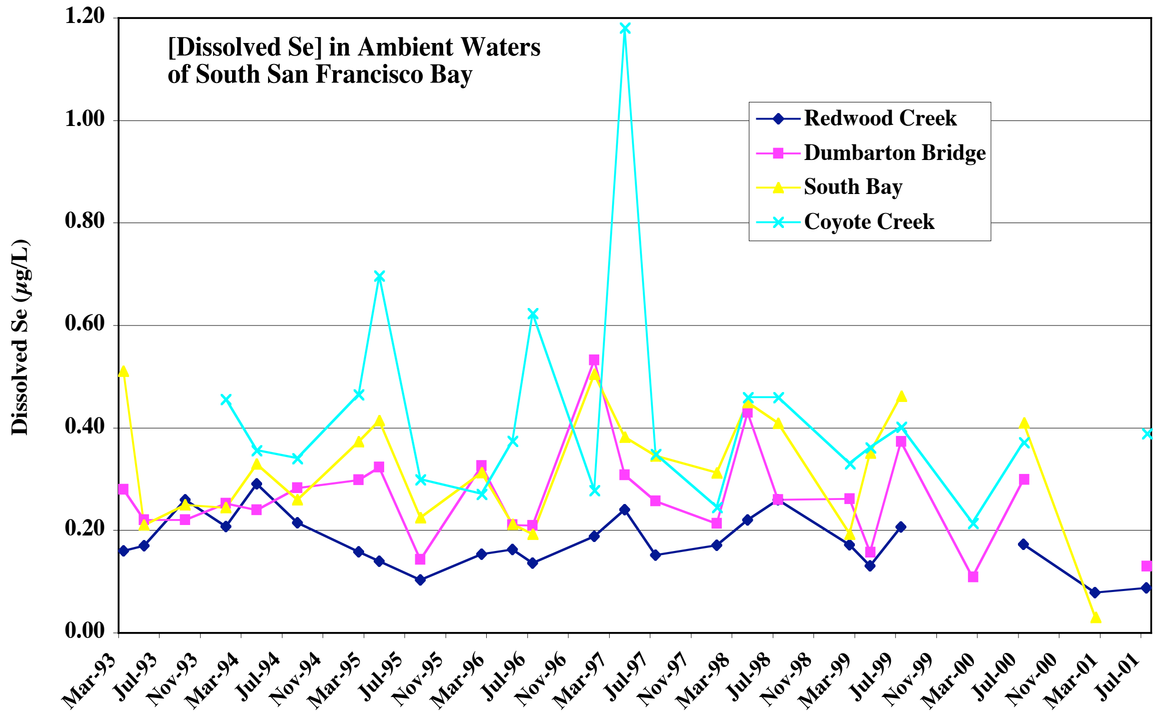


Figure 11. Ambient water selenium concentrations in northern San Francisco Bay. Data are from RMP (*http://www.sfei.org/rmp/data.htm*).



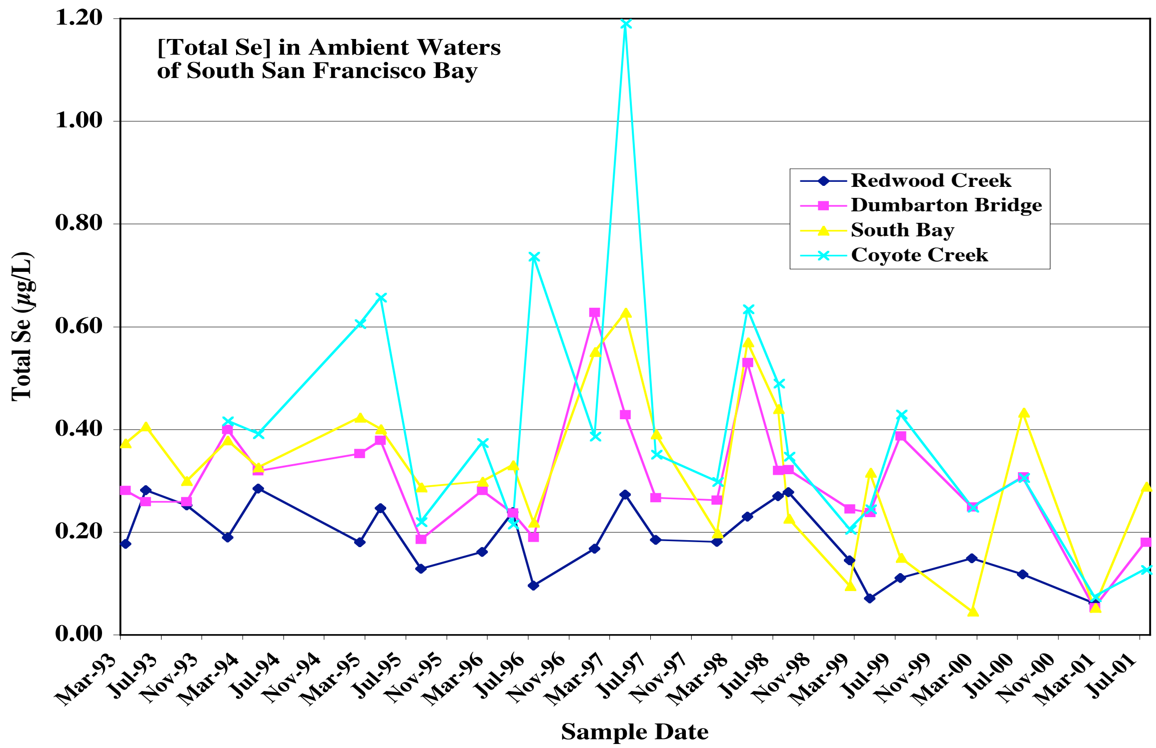


Figure 12. Ambient water selenium concentrations in South San Francisco Bay. Data are from RMP (*http://www.sfei.org/rmp/data.htm*).

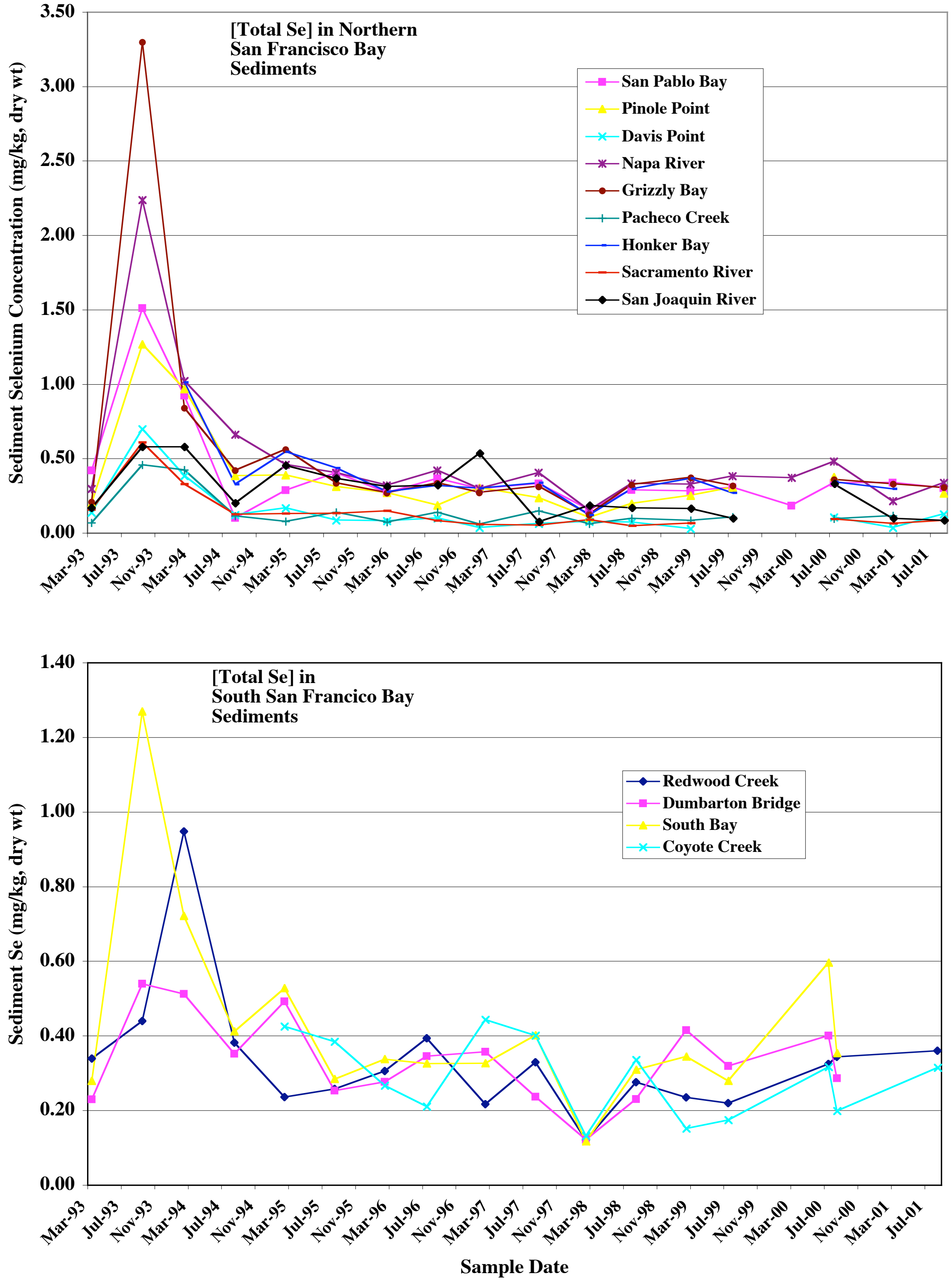


Figure 13. Ambient sediment selenium concentrations in Northern and South San Francisco Bay. Data are from RMP *(*http://www.sfei.org/rmp/data.htm*)*.

4.2 Health Advisory Against Consumption of Bay Organisms

The CA DOHS has provided the following health advisory warning for inclusion in the CA DFG 2004 Waterfowl Hunting Guidelines (personal communication: Dr. Margy Gassel, OEHHA):

> "The California Environmental Protection Agency's Office of Environmental Health Hazard Assessment (OEHHA) determines whether a public health hazard may exist from consumption of waterfowl taken from certain locations in California based on laboratory testing data. The following advisories have been issued. The guidelines are based on risk estimates that assume long-term consumption; thus, occasional intake of duck meat slightly above the recommended quantitative limits is not expected to produce a health hazard.
>
> <u>Suisun Bay (Contra Costa and Solano Counties)</u>
> Because of elevated selenium levels, no one should eat more than 4 oz. per week of (greater and lesser) scaup meat, or more than 4 oz. of scoter meat in any 2 week period. No one should eat livers of duck from the area.
>
> <u>San Pablo Bay (Contra Costa, Marin, Solano, Sonoma Counties)</u>
> Because of elevated selenium levels, no one should eat more than 4 oz. per week of Greater Scaup meat, or more than 4 oz. of scoter meat in any 2-week period from the Bay. No one should eat livers of duck from the area.
>
> <u>San Francisco Bay (Alameda, Contra Costa, Marin, San Francisco, San Mateo, Santa Clara Counties)</u>
> Because of elevated selenium levels, no one should eat more than 4 oz. per week of Greater Scaup meat from the Central Bay, or more than 4 oz. of Greater Scaup meat from the South Bay in any 2-week period. No one should eat livers of duck from the area".

4.3 Bay Protection and Toxic Cleanup Program Sites

The following 5 sites were placed on the 2002 303(d) list for selenium, presumably because they were BPTCP Category IV Sites:

Castro Cove – Selenium was identified as a contaminant of concern for Castro Cove as the measured sediment concentration exceeded the BPTCP 90th percentile value of 1.09 mg/kg and there was sediment toxicity to amphipods and sediment porewater toxicity to urchin embryos (Hunt et al. 1998). It is important to note that:

- there was no causal relationship established between the observed sediment toxicity and selenium,
- there were 11 other contaminants in this sediment that exceeded the ERM sediment quality risk threshold, and the sediment exhibited an ERM quotient of 2.25 (indicative of a high potential for toxicity due to one or more of these 11 other contaminants),
- The reported sediment selenium concentration of 2.03 mg/kg is less than the TMDL guidance maximum acceptable concentration of 4.0 mg/L established by USFWS

selenium experts (Lemly 2000).

Furthermore, the Castro Cove pollution problem is being remediated.

San Leandro Bay - Selenium was identified as a contaminant of concern for San Leandro Bay as the measured sediment concentration exceeded the BPTCP 90th percentile value of 1.09 mg/kg and there was sediment toxicity to amphipods (there was no sediment porewater toxicity to urchin embryos) (Hunt et al. 1998). It is important to note that:

- there was no causal relationship established between the observed sediment toxicity and selenium.
- there were 10 other contaminants in this sediment that exceeded the ERM sediment quality risk threshold, and the sediment exhibited an ERM quotient of 1.52 (indicative of a high potential for toxicity due to one or more of these 10 other contaminants).
- The reported sediment selenium concentration of 2.83 mg/kg is less than the TMDL guidance maximum acceptable concentration of 4.0 mg/L established by USFWS selenium experts (Lemly 2000).

Inner Oakland Harbor - Pacific Dry Dock – It is unclear why this site was listed for impairment due to selenium, as it was not identified as having elevated selenium concentrations by the BPTCP (Hunt et al. 1988). Furthermore, the initial indication of sediment toxicity to amphipods (there was no sediment porewater toxicity to urchins) at this site was compromised due to the observation of sulfide levels that exceeded the toxicity threshold. In addition, it is important to note that there was no causal relationship established between the observed sediment toxicity and selenium. In fact, there were 9 other contaminants in this sediment that exceeded the ERM sediment quality risk threshold, and the sediment exhibited an ERM quotient of 1.27 (indicative of a high potential for toxicity due to one or more of these 9 other contaminants).

Similarly, there was no causal relationship established between the observed sediment toxicity of the second sediment sample collected at this site and selenium. In fact, there were 22 other contaminants in the second sediment sample that exceeded the ERM sediment quality risk threshold, and the sediment exhibited an ERM quotient of 3.94 (indicative of a very high potential for toxicity due to one or more of these 22 other contaminants).

Inner Oakland Harbor – Fruitvale - It is unclear why this site was listed for impairment due to selenium, as it was not identified as having elevated selenium concentrations by the BPTCP (Hunt et al. 1988). Furthermore, the initial indication of sediment toxicity to amphipods (there was no sediment porewater toxicity to urchins) at this site was compromised due to the observation of sulfide levels that exceeded the toxicity threshold. In addition, it is important to note that there was no causal relationship established between the observed sediment toxicity and selenium.

Similarly, there was no causal relationship established between the observed sediment toxicity to amphipods (again, no toxicity to urchins) of the second sediment sample collected at this site and selenium. Furthermore, the indication of sediment toxicity to amphipods for the second sample collected at this site was even more compromised due to the observation of sulfide levels that exceeded the toxicity threshold *and* ammonia levels that were more than 5-fold greater than the toxicity threshold.

Central Basin - It is unclear why this site was listed for impairment due to selenium, as it was not identified as having elevated selenium concentrations by the BPTCP (Hunt et al. 1988). Furthermore, the initial indication of sediment porewater toxicity to urchins (there was no sediment toxicity to amphipods) at this site was compromised due to the observation of ammonia levels that exceeded the toxicity threshold. In addition, it is important to note that there was no causal relationship established between the observed sediment toxicity and selenium. In fact, there were 8 other contaminants in this sediment that exceeded the ERM sediment quality risk threshold.

4.3.1 Is Selenium Impairing the BPTCP Sites?

There is no indication that selenium is causing or contributing to any toxicity problems at these BTCP sites. In addition to the observations noted above, it is important to note that the reported acute LC_{50} for selenium toxicity to bivalve embryos (analogous to the BPTCP urchin embryos) is >10,000 μg/L (US EPA 2002), more than four orders of magnitude greater than the concentrations observed in the Bay's ambient waters. Similarly, the acute LC_{50} for the *most sensitive* crustacean (analogous to the sediment amphipod) is 600 μg/L (US EPA 2002), again multiple orders of magnitude greater than could reasonably be expected in Bay sediment porewaters. These toxicity data indicate that it is very unlikely that selenium is responsible for the toxicity that was observed at these sites.

4.4 Conclusion: Is Selenium Impairing San Francisco Bay?

Any assessment of impairment of the Bay's waters will by necessity be based upon a "weight of evidence" approach, with review and evaluation of all available relevant information. The Clean Estuary Partnership has proposed a set of potential conclusions and outcomes of impairment assessment that reflects the State's 303(d)-listing policy categorizations (Table 11). Based upon this current review of available information, it is this study's conclusion that:

> **There is *possible impairment* of the Bay by selenium –** The continued presence of a health advisory against the consumption of diving ducks in San Francisco Bay clearly meets the State Board's Category 4 classification that selenium does impair one or more of the beneficial uses of San Francisco Bay. However, there are some uncertainties that must be addressed with additional studies (see Section 5). As a result, it must be concluded that there is **possible impairment** of San Francisco Bay by selenium.
>
> **BPTCP Toxicity:** Based upon the overwhelming weight-of-evidence presented in Section 4.3 above, it is concluded that selenium is ***not*** impairing the BPTCP sites that were added to the 303(d) list in 2002, and "de-listing" these sites for impairment by selenium is warranted.

Table 11. Characterizations of the impairment of San Francisco Bay	
Clean Estuary Partnership Classification	State 303(d) Listing Policy Categories[a]
No Impairment – The available data are sufficient to unequivocally demonstrate that there are no negative effect(s) on the Bay's beneficial uses caused by selenium.	Category 1. Attaining the water quality standard and no use is threatened.
Impairment Unlikely – The available data indicate no negative effect(s) on beneficial uses of the Bay, however, there is some uncertainty due to lack of sufficient information or disagreement about how to interpret that data.	Category 2. Attaining some of the beneficial uses; no use is threatened; and insufficient or no data and information is available to determine if the remaining uses are attained or threatened.
Unable to Determine Impairment – There is insufficient information to make any determination.	Category 3. Insufficient or no data and information to determine if any designated use is attained.
Possible Impairment – The available data suggest that there may be impairment of the Bay's beneficial uses caused by selenium, however there are some uncertainties that must be addressed with additional studies.	
	Category 4. One or more beneficial uses are threatened, but the development of a TMDL is not required.
Definite Impairment – The available data are sufficient to clearly demonstrate that there are negative effect(s) on the Bay's beneficial uses caused by selenium.	Category 5. The water quality standard is not attained.

a – SWRCB 2003.

5. Uncertainties and Data Gaps

5.1 Uncertainties Associated with the 1998 303(d) Listings

Any objective analysis will always contain uncertainties. A summary of uncertainties is an important component of the impairment assessment, as the uncertainties guide subsequent investigations.

5.1.1 Appropriate Calculation of Dietary Exposures

In calculating the amount of duck tissue that could safely be consumed, the DOHS used the following formula:

$$PI = \frac{ADI - DI}{C}$$

Where	PI	= permissible intake of duck flesh
	ADI	= acceptable daily intake, = 210 μg/day
	DI	= Daily dietary selenium uptake, = 170 μg/day
	C	= concentration of selenium in duck flesh

When DOHS did their original calculations, an Agency for Toxic Substances and Disease Registry (ATSDR, an agency of the U.S. Department of Health and Human Services) Minimal Risk Level (MRL) was not available; the MRL is a daily intake that ATSDR considers to be safe for all populations. However, the ATSDR recently established an MRL of 5 μg/kg/day for chronic oral exposure (daily consumption, for the life of the individual) (ATSDR 2003). This MRL is based upon a No Observable Adverse Effect Level (NOAEL - the highest dose at which no statistically or biologically significant adverse effects were observed) of 15 μg/kg/day. For a 70 kg adult, this is equivalent to a selenium intake of 1,050 μg/day. To establish the MRL, ATSDR divided the NOAEL by a factor of three to account for human variability and arrived at 5 μg/kg/day, which corresponds to 350 μg/day for a 70 kg individual.

Replacing the CA DOHS ADI with the ATSDR MRC of 350 μg/day results in a 66% increase in the amount of duck tissue that could be consumed. Replacing the CA DOHS ADI with the No Observable Adverse Effect Level of 1,050 μg/day results in a 400% increase in the amount of duck tissue that could be consumed.

Moreover, there remains some question as to whether or not there is enough consumption of these ducks to warrant such concern. Anecdotal information suggests that these diving ducks are hunted primarily for sport, and are not eaten due to the fact that they taste bad. DOHS reported that the Surf Scoter "is seldom shot for food, since its flesh has a strong flavor that is very disagreeable to most people. Its lack of palatability … renders it of slight importance as a game bird" (Fan and Book 1986). It was also reported that "scaups are among the less desirable of ducks for table use because their flesh is tainted by their shellfish diet."

It seems clear that the actual risk posed by the potential consumption of these diving dicks is in need of re-evaluation, taking into account the most recent selenium exposure health information, and arguably a probabilistic assessment that includes the actual likelihood of consumption.

5.2 Compliance with US EPA's Draft Selenium Criteria

In 2004, the US EPA released a Draft Aquatic Life Criteria for Selenium that proposed a fish whole-body tissue selenium concentration of 7.91 μg/g, dry wt, as the chronic toxicity limit (US EPA 2004), with recommendations to monitor the status of the fish community if the tissue selenium concentration exceeds 5.85 μg/g.

Using the US EPA's Draft Selenium Criteria formula for converting muscle selenium concentration to whole body selenium concentration, the most recent sturgeon muscle data (from 2003-2004 [Linares et al. 2004]) correspond to a mean of 6.1 μg/g, whole body dry wt, indicating that the mean sturgeon tissue selenium concentrations are within the proposed chronic criterion of 7.91 μg/g, dry wt (US EPA 2004). However, this does exceed the EPA's monitoring recommendation limit of 5.85 μg/g, indicating that monitoring of the status of the sturgeon population may be warranted.

Unfortunately, considerable disagreement with EPA proposed fish tissue criterion of 7.91 μg/g was expressed by other resource agencies during the Endangered Species Act consultation process. While the status of the draft criteria on a national basis remains unclear, the US EPA, US FWS, USGS, NMFS, and State Board met in September 2002, and agreed develop California-specific (via the California Toxics Rule [CTR]) water quality criteria that would protect not only aquatic life, but also other federally-listed threatened and endangered species (Grubbs and Kuhlman, 2002). A contract was recently issues to the USGS to complete the development of two criteria:

1) A criterion for California in general, using the Great Lakes Initiative (GLI) Wildlife Methodology (40 CFR Part 132), which was used to derive the proposed national fish tissue criterion of 7.9 μg/g, but with input from other resource agency scientists in the new derivation of a numerical limit.
2) A criterion specifically for the San Francisco Estuary watershed using the selenium risk assessment model of Luoma and Presser (2000) This model is specific to selenium loadings and ecosystem effects in the Sacramento-San Joaquin River Delta.

5.3 Other Potential Impairments

5.3.1 Potential Impairment of Diving Duck Reproduction

Although the original regulatory listings for selenium in the Bay were not about the health of wildlife so much as the health of people who hunt and eat diving ducks for food, it is important to note that questions have been raised as to how selenium in the Bay's food web affects the breeding success of migratory birds. Preserving wildlife habitat and making sure that game species are of food-quality are both important to the Bay Area economy. There are over 200 private duck hunting clubs around Suisun Bay and the Bay-Delta. The US Fish and Wildlife Service estimates that duck hunters bring over $100 million to the State annually (San Francisco Estuary Project, 1992). Businesses and tourism enterprises that serve duck hunters depend on the successful annual return of migratory waterfowl such as the Surf Scoter.

The successful breeding and return of migratory birds is also critical to protecting public investments in the Baylands surrounding San Francisco Bay. The Baylands draw over 100,000 visitors every year. Much of the Baylands access and display infrastructure is devoted to bird-watching and public education about migratory birds. Judging by the level of investments made, it is clear that the Bay Area public greatly values protection of the beneficial use of wildlife habitat [see for example, (City of Palo Alto, 2002)].

Tracking the reproductive success of migratory waterfowl that pass through the Bay is problematic in that their breeding grounds are typically elsewhere (e.g., in Alaska and Canada). However, birds that have accumulated selenium in San Francisco Bay should be expected to rapidly lose that selenium upon their departure from the Bay (Heinz et al. 1990); studies have indicated that the selenium concentration in waterfowl eggs responds extremely rapidly to maternal dietary exposure, with egg selenium levels falling from as high as >20 ppm to <3 ppm (a level predicted to have no effects on reproduction [Lemly 2002]) within 12-16 days after the maternal selenium exposure ends (Heinz 1993). These studies indicate that any potential reproductive impairment of these diving ducks may be negligible within a week or two of leaving the Bay.

An assessment of any adverse effects of selenium on the reproduction of these diving ducks is even further complicated by the fact that they will have also been exposed to (and presumably accumulated) the mercury, PCBs, and legacy organochlorine pesticides that are known to contaminate San Francisco Bay, and/or that there are additional factors that could explain or contribute to diminished populations of migratory waterfowl including degraded boreal forest habitat in breeding grounds and staging areas.

5.3.2 Potential Impairment to Clam-Eating Fishes

The Asian clam, *Potamocorbula amurensis*, that invaded the estuary in the mid-1980s is a highly efficient selenium accumulator, and exacerbated selenium bioaccumulation in benthic predators is not limited to diving ducks, but may also extend to other bivalve consumers, including white sturgeon and Sacramento splittail (Urquhart et al. 1991; Stewart et al. 2004).

San Francisco Bay white sturgeon samples in 1986 and 1990 exhibited liver selenium concentrations of 9-30 μg/g dry wt, and muscle selenium concentrations of 7-17 μg/g, dry wt (White et al. 1988; Urquhart et al. 1991); however, the concentrations measured since have declined from the apparent peak in 1990 (Figure 14). As reported previously, the most recent sturgeon muscle selenium data corresponds to a mean whole body selenium concentration of 6.1 μg/g; this is below the EPA's 7.91 μg/g limit, but slightly above the monitoring threshold of 5.85 μg/g, indicating that monitoring of the status of the sturgeon population may be warranted. It has been hypothesized that white sturgeon in San Francisco Bay may be experiencing some type of impairment (Stewart 2004), and CALFED studies to address this hypothesis are underway.

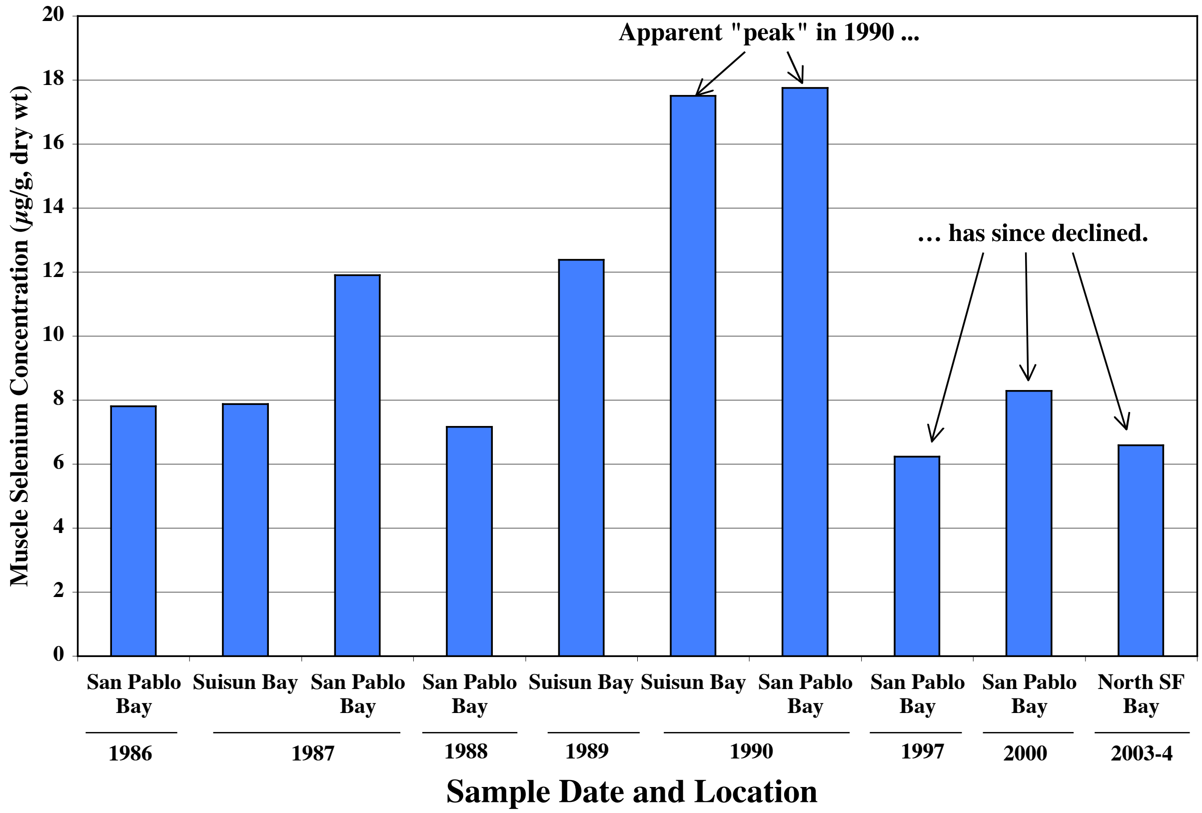


Figure 14. Selenium concentrations (μg/g, dry wt) in white sturgeon muscle tissue. Data from the Selenium Verification Study (White et al. 1988; Urquhart et al. 1991), the RMP data set, and Linares et al. (2004).

While a similar long-term data set for selenium concentrations in Sacramento splittail are not available, their benthivorous diet as adults includes *Potamocorbula amurensis* (Feyrer et al. 2003) indicating that they are similarly exposed to elevated selenium concentrations in their food. However, the Sacramento splittail tissue selenium concentrations are markedly less than seen in white sturgeon, and are more similar to those seen in striped bass (see Figure 2 in Stewart et al. 2004). Nevertheless, it has been reported that exposure to dietary selenium may cause physical deformities in splittail (Teh et al. 2004), although statistical analyses of these data failed to reveal any dose-response relationship; similar deformities have been observed in wild-caught splittail (Stewart et al. 2004), suggesting that selenium may be adversely affecting the splittail.

5.3.3 Use of Impairment or Risk Threshold Guideline Values

Numeric indicators help to quantify the status of the Bay with respect to different pollutants. Just as the California Highway Patrol uses the speed limit as a numeric indicator for unsafe driving, concentrations of selenium in water, sediment, and organisms are important numeric indicators that tell us whether or not selenium impairs the beneficial uses of fishing (COMM), wildlife habitat (WILD), or protection of rare and endangered species (RARE). Just as the Highway Patrol use multiple numeric indicators to identify unsafe driving (e.g., speed, following distance, blood alcohol concentration), the multiple numeric indicators summarized in Table 12 provide additional detail on not just whether the Bay is impaired, but also how.

What we know for sure is that the Bay is in attainment of numeric indicators in water and sediments, and over numeric indicators for key prey species (*P. amurensis)*, as well as indicators for organismal exposure (bird livers). We don't know if human consumers are at risk – there is a consumption advisory, but because of the narrow window between nutritional requirement and toxicity and the use of questionable parameters in the health risk calculations, there are some questions about the original risk assessment.

We also don't have definitive evidence for effects on reproductive success of wildlife in the Bay due to selenium in the food chain, in part because many of the species we are most concerned about don't reproduce in the Bay, they just eat there. We do know that selenium concentrations in exposed organisms that feed heavily on benthic invertebrates exceed teratogenic thresholds found in other ecosystems, so we have reason to be concerned.

Table 12. Current status of indicators of beneficial use impairment by selenium in San Francisco Bay			
Indicator	Relation to Beneficial Uses	Threshold	Status of the Bay
Water	Indicator of chronic toxicity	5 µg/L	**GOOD** – most of the Bay 0.02-0.6 µg/L , average 0.2 µg/L. Low-flow exceedances up to 9 µg/L observed in southern estuary interface at Alviso Slough.
Sediments	Particles are major pathway for bioaccumulation	4 µg/g (dry wt)	**GOOD** – most of the Bay 0.01-0.6 µg/g, average 0.3 µg/g. Episodic excursion as high as 3 µg/g observed in 1993; Napa Salt Ponds have 1-3 µg/g Se; condition of South Bay salt ponds unknown.
Bivalve Prey	Most significantly impacted branch of aquatic food web	3 µg/g (dry wt)	**BAD** – *P. Amurensis* levels ranged from 4-20 µg/g in 1990-96. Species has become significant food source to benthic predators.
Bird Livers	Indicator of organismal exposure	10 µg/g (dry wt)	**BAD** – While many species below threshold, scaups (average 36 µg/g) and scoters (13-368 µg/g, average 134 µg/g) well over this indicator; however, these concentrations are expected to drop rapidly once these birds leave the Bay.
Fish Livers	Indicator of organismal exposure	12 µg/g (dry wt)	**BAD** – Sturgeon livers in 1990-96 averaged 30 µg/g, with a range of 8-80 µg/g.
Fish eggs	Indicator of threats to reproductive success	10 µg/g (dry wt)	**BAD** – White sturgeon ovaries ranged from 3-29 µg/g in 1991, however subsequent decline in concentrations commensurate with those observed in muscle tissues should be expected.
Fish Muscle	Indicator of exposure risk to human	7.9 *µ*g/g (whole body dry wt)	**UNCERTAIN** – Magnitude and frequency of exceedances by sturgeon significantly diminished since 1991; risk assessment needs to be reviewed.
Bird Muscle	Indicator of exposure risk to human consumers	2 µg/g (dry wt)	**UNCERTAIN** – only liver concentration data appear to be available; need to verify if liver data were used to posit risk to humans; risk assessment needs to be reviewed.
Bird eggs	Indicator of threats to reproductive success	3 µg/g (dry wt)	**UNCERTAIN** – scant, preliminary data available, many migratory species nest far north of SF Bay in Alaska, Northwest Territories, and bird tissue concentrations drop rapidly after the end of any exposure.

a – California Toxics Rule.
Threshold values from: Fan et al. (1988); Lemly (1993, 1995, 2000); Van derVeer and Canton (1997); Hamilton and Lemly (1999), Luoma and Presser (2000), US EPA (2002), and the California Toxics Rule (CTR). Status from analysis of RMP data for this report, and as reported by Luoma and Presser (2000), and references cited therein.

5.4 Future Loadings of Agricultural Drainwater

Selenium loads from agricultural drainage are measured, modeled, and estimated based on concentrations and flows discharged from the agricultural management subareas of the San Joaquin Valley.

Future agricultural drainage loads may change dramatically, based on forecast scenarios for different drainage alternatives (Luoma and Presser, 2000). The extremely wide range in potential future loads from agricultural drainage results from the uncertainties about future disposal alternatives (in-Valley, to the Delta via the San Luis Drain, or direct drainage to the Pacific Ocean via a new drain). At present, in-valley disposal appears to be the preferred alternative, but this matter is not yet resolved (USBR, 2004). The "possible" future loading rate of 20,000 kg/yr is a speculative worst-case scenario. Ongoing selenium treatment operations may be as effective in reducing agricultural drainage loads as the oil refineries' implementation of selenium removal treatments were in reducing refinery loading.

But simply putting the Bay's selenium inventories and loads on scale with the upstream inventory of selenium in subsurface agricultural drains helps understand that any plans to extend agricultural drainage to the Bay could overwhelm its assimilative capacity (Figure 15).

An important qualifier in the mass load estimates for the San Joaquin River is that they reflect loads to the delta before diversions into the California Aqueduct, recycling into the Delta Mendota Canal and other water appropriation projects. This issue is under investigation by the United States Bureau of Reclamation, and represents another potentially important management question.

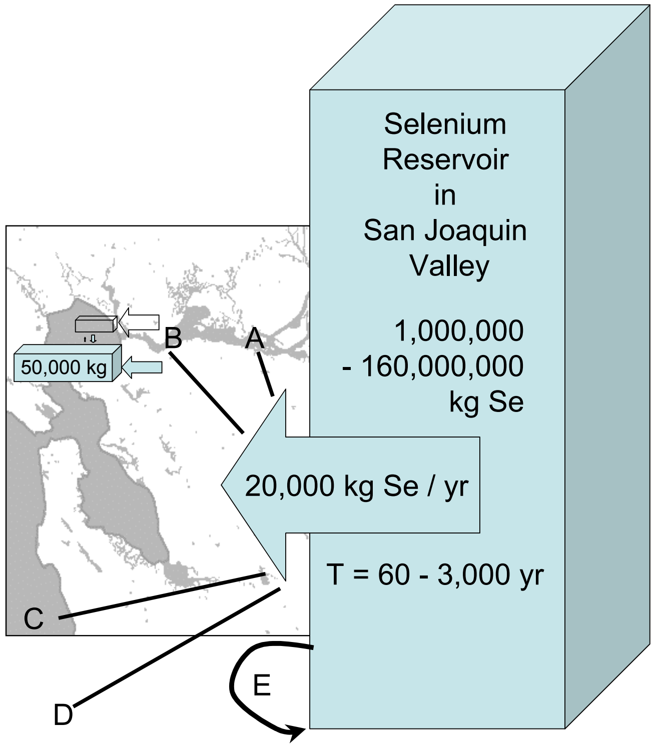


Figure 15. Conceptual illustration of why drainage plans from the San Joaquin Valley could threaten the Bay's assimilative capacity for selenium. The 50,000 kg sediment inventory from the 2-box model in Figure 7 is shown next to the multi-million kg selenium inventory of the San Joaquin Valley. To provide adequate drainage, 20,000 kg of selenium needs to be discharged for 60 – 3,000 years. Discharge points contemplated include San Francisco Bay (A – B) the Pacific Ocean (C – D) and "In-Valley" disposal (E, tentatively the preferred alternative identified by the USBR). The relative volumes of the boxes representing upstream and in-Bay inventories are scaled to relative selenium inventories (i.e., the volume of the upstream box is approximately 400 times greater than the in-Bay box).

6. Where Do We Go From Here: Filling the Information Gaps

This section summarizes the uncertainties in this report's conclusions and suggests some potential future projects to obtain additional data and conduct more analysis of the sources, fate, transport, and effects of selenium. In other documents or forums, the CEP will develop appropriate strategies for addressing selenium in the Bay and its watersheds. These strategies may include:

- Data collection or analysis,
- Implementation of corrective actions,
- Formulating and refining management questions and setting priorities for the above 2 activities,
- Determining an ongoing process for integrating all of the above.

There may be control measures, remediation, and regulatory actions that can and should begin now, even with existing uncertainties. CEP partners are committed to identifying these actions. Future CEP data gathering and technical analysis should focus on determining the potential effectiveness, and actual effects, of actions to reduce or eliminate impairment and to restore beneficial uses of the Bay.

Water Quality Planning and CEP Workplan Development

The State of California has developed a four-phased approach to resolving water quality impairments (California State Water Resources Control Board, 2003). Although this approach was developed well after substantial selenium monitoring and management strategies had been implemented in the Bay, it is possible to frame the past two decades of planning and action (i.e., the events summarized in Appendix A) in the four-phased approach (Figure 16). Within that framework, this report represents a review and analysis stage at the end of and adaptive implementation cycle, and prior to initiating another iteration of planning, analysis, action, and implementation.

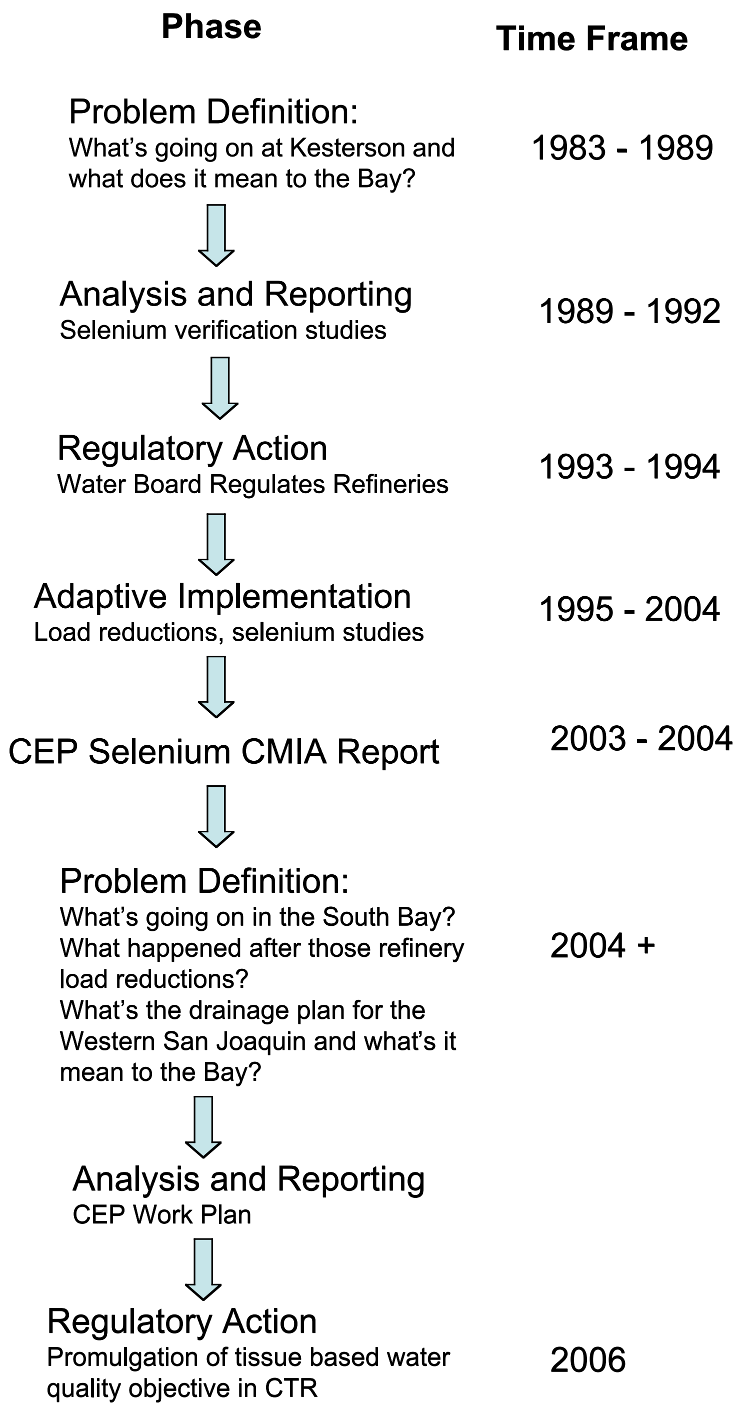


Figure 16. Context of this selenium Conceptual Model Impairment Assessment Report within the State's adaptive strategy for implementing water quality standards and the CEP's workplan development.

6.1 Function of this report in the CEP work plan

As a program supporting water quality standards implementation, the CEP invests resources in studies needed to develop science-based management plans. Funding priorities are set by the Technical Committee (TC), which recommends appropriation of funds for specific technical projects to the Administrative Committee. To ensure that resources are focused on the CEP program goals, the TC has established a process for scoping and funding projects (Figure 17).

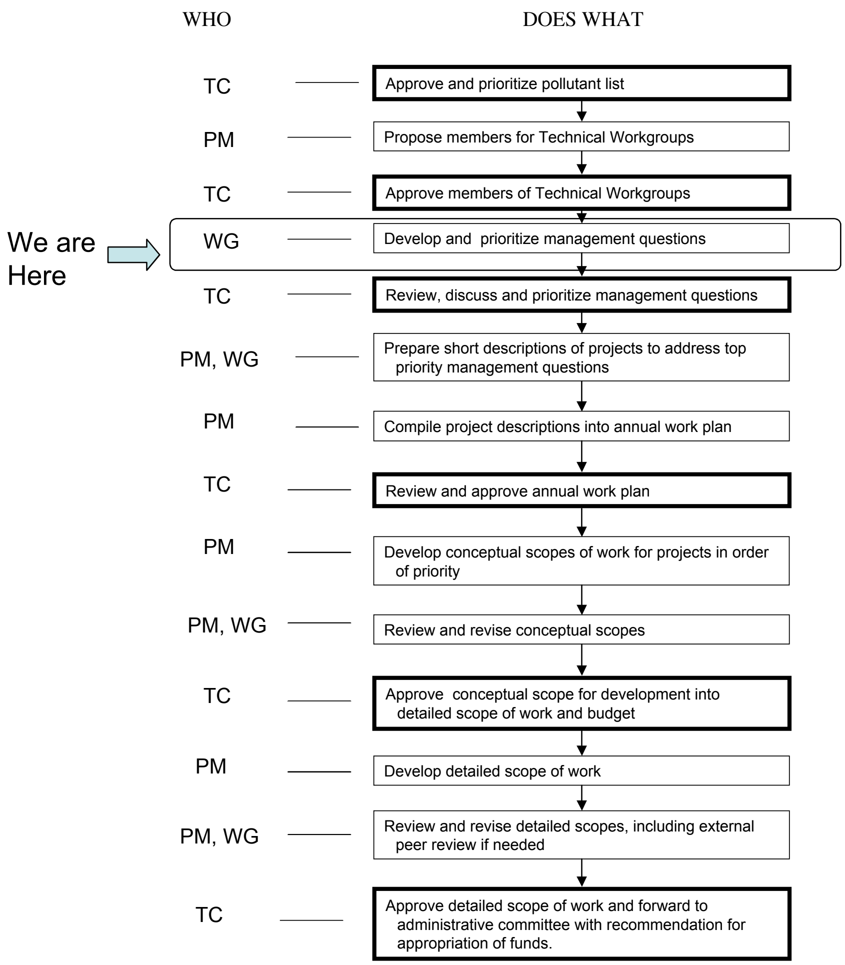


Figure 17. The CEP Technical Committee's process for developing, reviewing, and funding technical projects. PM = Program manager; TC = Technical Committee, WG = Selenium Workgroup

A list of high priority pollutants of concern is developed by the TC and approved by the CEP's Executive Management Board (EMB). Pollutant-specific workgroups of the TC develop questions about managing the Bay's assimilative capacity. Those management questions are prioritized, and the highest priority questions are developed into project descriptions for the annual work plan. The annual work plan is implemented by developing conceptual scopes from each project description, reviewing and revising the conceptual scopes, and upon approval by the TC, production of detailed scopes of work that are funded by the EMB and executed under supervision of the TC and its workgroups and staff.

Within that process, this report takes the CEP TC to the stage of developing, ranking, and prioritizing management questions for selenium. Those management questions are discussed in the last section of this report.

A preliminary list of management questions raised by this report is presented in Table 13.

Table 13. Preliminary list of selenium management questions identified in this report		
Management Question	**Relevant report sections**	**General approach to answering it**
Does selenium bioaccumulation in the Bay affect the breeding success of migratory birds?	Section 5.3.1	Coordination with resource agencies (e.g., USFWS, CDFG) and national wildlife organizations.
Does selenium bioaccumulation in these diving ducks pose a threat to human consumers?	Section 5.1	Literature review, coordination with OEHHA, environmental groups, probabilistic risk assessment
Are San Francisco Bay fish tissue selenium concentrations in compliance with the DRAFT 2002 EPA criteria?	Section 5.2	Literature review, and possible development of model to correlate liver and muscle concentrations to whole-body concentrations.
Are the selenium concentrations in white sturgeon and Sacramento splittail impairing the wild populations of these fish in SF Bay?	Section 5.3.2	Continue to monitor the results of ongoing CALFED studies
Will the Bay's waters, sediments, and/or organism tissue selenium concentrations be in compliance with the new criteria currently under development?	Section 5.2	Coordination with the resource agencies (e.g., USEPA, USGS) developing the new criteria.
What causes the extremely high selenium concentrations observed at Alviso Slough?	Sections 3.2.4	Investigation of groundwater discharges
How do water management choices, including flood control, salt pond management, dry weather reclamation, and groundwater recharge affect selenium concentrations and distributions in lower South Bay?	Sections 3.2.4	Coordination with external programs and projects (e.g., SANTA Clara Basin WMI, South Bay Salt Ponds long term management plan development)
How does freshwater diversion from the Delta affect the net effect of selenium discharges to the Bay from the San Joaquin River?	Section 3.1	Coordination with USBR
How will increases in the flow of San Joaquin River water though the Delta and northern San Francisco Bay affect selenium bioaccumulation by the Bay's foodweb?	Sections 3.2 and 3.3.2.3	Coordination with water resource agencies, and application of USGS and CALFED-study models.

Table 13 (continued): Preliminary list of selenium management questions identified in this report.		
Management Question	**Relevant report sections**	**General approach to answering it**
Are average selenium concentrations in Bay Area municipal water supply, effluent, urban and non-urban streams more like 0.1 μg/L or 1.0 μg/L?	Section 3.2.8.3	Additional data gathering and synthesis, targeted subsampling of different water source types for accurate low-level analysis
How do pollutant partition coefficients affect distributions and recovery time scales, especially in Lower South Bay?	Sections 3.2 – 3.3	Synthesis and peer review of existing data in coordination with CEP modeling project.
How will alternatives to provide agricultural drainage under consideration by the United States Bureau of Reclamation affect future selenium loads to the Bay?	Sections 5.4	Coordinate with USBR, upstream stakeholders, resource agencies

7. References Cited

Abu-Saba KE (2003) DRAFT Mercury Source Assessment for San Francisco Bay, San Francisco Bay Clean Estuary Partnership, Oakland, California.

Abu-Saba KE, Tang LW (2000) Watershed Management of Mercury in San Francisco Bay: a TMDL report to the USEPA, San Francisco Bay Regional Water Quality Control Board. California Environmental Protection Agency. San Francisco Bay Regional Water Quality Control Board, Oakland, California, pp. 170.

Alaimo J, Ogle RS, Knight AW (1994) Selenium uptake by larval *Chironomus decorus* from a Rupee maritima-based benthic/detrital substrate. Archives of Environmental Contamination & Toxicology, 27(4): 441-448.

Alpine AE, Cloern JE (1992) Trophic interactions and direct physical effects control phytoplankton biomass and productivity in an estuary. Limnology and Oceanography 37:946-955.

Amoroux D, Donard OFX (1997) Evasion of selenium to the atmosphere via biomethylation processes in the Gironde estuary, France. Marine Chemistry 58:173-188.

Ansede JH, Yoch DC (1997) Comparison of selenium and sulfur volatilization by dimethylsulfoniopropionate lyase (DMSP) in two marine bacteria and estuarine sediments. FEMS Microbiology Ecology 23:315-324.

Arthur JF, Ball MD (1979) Factors influencing the entrapment of suspended material in the San Francisco Bay-Delta Estuary. Pages 143-174 in: Conomos TJ (ed), San Francisco Bay: The urbanized Estuary. Pacific Division, American Association for the Advancement of Science, San Francisco, CA.

ATSDR (2003) Toxicological Profile for Selenium. Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services, Washington, D.C.

Bailey FC, Knight AW, Ogle RS, Klaine SJ (1995) Effect of sulfate level on selenium uptake by *Ruppia maritima*. Chemosphere, 30(3): 579-591.

Baines SB, Fisher NS (2001) Interspecific differences in the bioconcentration of selenite by phytoplankton and their ecological implications. Marine Ecology Progress Series 213:1-12.

Baines SB, Fisher NS, Doblin MA, Cutter GA (2001) Uptake of dissolved organic selenides by marine phytoplankton. Limnology & Oceanography, 46(8): 1936-1944.

Baines SB, Fisher NS, Stewart R (2002) Assimilation and retention of selenium and other trace elements from crustacean food by juvenile striped bass (*Morone saxatilis*). Limnology Oceanography 47(3):646-655.

Baines SB, Fisher NS, Doblin MA, Cutter GA, Cutter LS, Cole B (2004) Light dependence of selenium uptake by phytoplankton and implications for predicting selenium incorporation into food webs. Limnology Oceanography 49(2):566-578.

Balistrieri LS, Chao TT (1990) Adsorption of selenium by amorphous iron oxyhydrooxides and manganese dioxide. Geochimica Cosmochimica Acta 54:739-751.

Besser JM, Huckins JN, Clark RC (1994) Separation of selenium species released from Se-exposed algae. Chemosphere 229:771-780.

Boisson F, Gnassia-Barelli M, Romeo M (1995) Toxicity and accumulation of selenite and selenate in the unicellular marine alga *Cricospaera elongata*. Archives Environmental Contamination Toxicology 28:487-493.

Bottino NR, Banks C, Irgolic KJ, Micks P, Wheeler AE, Zingaro RA (1984) Selenium-containing amino acids and proteins in marine algae. Phytochemistry 23(111):2445-2452.

Brasher AM, Ogle RS (1993) Comparative toxicity of selenite and selenate to the amphipod *Hyalella azteca*. Archives of Environmental Contamination & Toxicology, 30: 274-279.

Brown CL, Luoma SN (1995) Use of the euryhaline bivalve *Potamocorbula amurensis* as a biosentinel species to assess trace metal contamination in San Francisco Bay. Marine Ecology Progress Series 124(1-3): 129-142.

CA OEHHA (1987) Duck Consumption Advisory for Suisun Bay, San Pablo Bay, and the Carquinez Straits, CAL-EPA, Office of Environmental Health Hazard Assessment, Sacramento, CA.

California State Water Resources Control Board (2003) DRAFT State of California S.B. 469 TMDL Guidance: A process for Addressing Impaired Waters in California, California State Water Resources Control Board, Sacramento, CA.

Carlton JT, Thompson JK, Schemel LE, Nichols FH (1990) The remarkable invasion of San Francisco Bay, California, by the Asian clam *Potamocorbula amurensis*: introduction and dispersal. Marine Ecology Progress Series.

Chapman PM (1999) Selenium - A potential time bomb or just another contaminant? Human & Ecological Risk Assessment, 5(6): 1123-1138.

City of Palo Alto (2002) Adoption of a Resolution Authorizing the City Manager to Apply for a Grant and Execute an Agreement with their State of California for a Roberti-Z'berg-Harris Urban Open Space and Recreation Grant for Improvements to Parking Lots at the

Baylands, Palo Alto City Council. Palo Alto City Council. City of Palo Alto, Palo Alto, CA.

Combs GF (2001) Selenium in global food systems. British Journal of Nutrition, 85(5): 517-547.

Conomos TJ (1979) Properties and Circulation of San Francisco Bay Waters. In: T.J. Conomos (Editor), San Francisco Bay: The Urbanized Estuary. Pacific Division, American Association for the Advancement of Science, San Francisco, pp. 493.

Coyle JJ, Buckler DR, Ingersoll CG, Fairchild JF, May TW (1993) Effect of dietary selenium on the reproductive success of bluegills (*Lepomis macrochirus*). Environmental Toxicology and Chemistry 12:551-565.

Cutter GA, Bruland KW (1984) The marine biogeochemistry of selenium: a re-evaluation. Limnology Oceanography 29:1179-1192.

Cutter GA (1989) The estuarine behavior of selenium in San Francisco Bay. Estuarine, Coastal and Shelf Science, 28(1): 13-34.

Cutter GA, San Diego-McGlone MLC (1990) Temporal variability of selenium fluxes in San Francisco Bay. Science of the Total Environment 97/98: 235-250.

Cutter GA, Cutter LS (1998) Metalloids in the high latitude North Atlantic: sources and internal cycling. Marine Chemistry 61:25-36.

Cutter GA, Cutter LS (2004) Selenium biogeochemistry in the San Francisco Bay estuary: changes in water column behavior. Estuarine Coastal Shelf Science 61:463-476.

Davis J, (2004) The Long Term Fate of PCBs in San Francisco Bay, San Francisco Estuary Institute, Oakland, California.

Doblin MA, Baines SB, Cutter LS, Cutter GA (2005) Selenium biogeochemistry in the San Francisco Bay estuary: Seston and phytoplankton. Manuscript in review, Estuarine, Coastal, and Shelf Science.

Dowdle PR, Oremland RS (1998) Microbial oxidation of elemental selenium in soil slurries and bacterial cultures. Environmental Science & Technology 32(23): 3749-3755.

Fan AM, Book SA (1986) Human health significance of selenium in scoters and scaups in San Francisco Bay Region. CA OEHHA, Dept. of Health Services, Berkeley, CA.

Fan AM, Lipsett MJ (1988) Human health evaluation of findings on selenium in ducks obtained from the Selenium Verification Study 1986-1987: Update of health advisories. CA Dept. of Health Services, Hazard Evaluation Section, Berkeley, CA.

Fan AM, Book SA, Neutra RR, Epstein DM (1988) Selenium and human health implications in California's San Joaquin Valley. Journal of Toxicology and Environmental Health 23: 539-559.

Fisher NS, Reinfelder JR (1991) Assimilation of selenium in the marine copepod *Acartia tonsa* studies with a radiotracer method. Marine Ecology Progress Series 70157-164.

Fisher NS, Wente M (1993) The release of trace elements by dying marine phytoplankton. Deep Sea Research 40:671-694

Foda A, Vandermeulen J, Wrench JJ (1983) Uptake and conversion of selenium by a marine bacterium. Canadian Journal Fisheries and Aquatic Sciences 40(supplement 2):215-220.

Fowler SW, Benayoun G (1976) Influence of environmental factors on selenium flux in two marine invertebrates. Marine Biology 37:59-68.

Greenfield BK et al. (2003) Contaminant concentrations in fish from San Francisco Bay, 2000, San Francisco Estuary Institute, Oakland, CA.

Grovhoug T, Lau G, Abu-Saba KE (2004) Mercury Management by Bay Area Wastewater Treatment Plants, San Francisco Bay Clean Estuary Partnership, Oakland, California.

Guo L, Frankenberger WT, Jury WA (1999) Evaluation of simultaneous reduction and transport of selenium in saturated soil columns. Water Resources Research 35(3):663-669.

Hamilton SJ, Lemly AD (1999) Water-sediment controversy in setting environmental standards for selenium. Ecotoxicology & Environmental Safety 44(3): 227-235.

Hansen D, Duda PJ, Zayed A, Terry N (1998) Selenium removal by constructed wetlands - role of biological volatilization. Environmental Science & Technology 32(5): 591-597.

Harrison PJ, Yu PW, Thompson PA, Price NM, Phillips DJ (1988) Survey of selenium requirements in marine phytoplankton. Marine Ecology Progress Series 47:89-96.

Harvey TE (1992) Status and trends report on wildlife of the San Francisco Estuary, San Francisco Estuary Project, Oakland, CA.

Heinz GH, Hoffman DJ, Gold LG (1989) Impaired reproduction of mallards fed an organic form of selenium. Journal of Wildlife Management 53(2):418-428.

Heinz GH, Pendleton GW, Krynitsky AJ, Gold LG (1990) Selenium accumulation and elimination in mallards. Archives Environmental Contamination and Toxicology 19:374-379.

Heinz GH (1993) Selenium accumulation and loss in mallard eggs. Environmental Toxicology and Chemistry 12:775-778.

Hu MH, Yang YP, Martin M, Yin , Harrison PJ (1997) Preferential uptake of Se(IV) over Se(VI) and the production of dissolved organic Se by marine phytoplankton. Marine Environmental Research 44:225-231.

Hunt JW, Anderson BS, Phillips BM, Newman J, Tjeerdema RS, Taberski KK, Wilson CJ, Stephenson M, Puckett HM, Fairey R, Oakden J (1998) Sediment quality and biological effects in San Francisco Bay. Bay Protection and Toxic Cleanup Program. Final Technical Report. San Francisco Bay Regional Water Quality Control Board, Oakland, CA.

Johns C, Luoma SN, Elrod V (1998) Selenium accumulation in benthic bivalves and in fine sediments of San Francisco Bay, the Sacramento-San Joaquin Delta, and selected tributaries. Estuarine Coastal Shelf Science 27:381-396.

Johnson TM, Bullen TD, Zawislanski PT (2000) Selenium stable isotope ratios as indicators of sources and cycling of selenium: results from the northern reach of San Francisco Bay. Environmental Science Technology 34:2075-2079.

Kim K, Kayes TB, Anundson CH (1992) Requirements for sulfur amino acids and utilization of d-methionine by rainbow trout (*Oncorhynchus mykiss*). Aquaculture 101:95-103.

Lehman PW (2000) The influence of climate on phytoplankton community carbon in San Francisco Bay estuary. Limnology and Oceanography 45:580–590.

Lemly AD (1993) Guidelines for evaluating selenium data from aquatic monitoring and assessment studies. Environmental Monitoring & Assessment, 28(1):83-100.

Lemly AD (1995) A protocol for aquatic hazard assessment of selenium. Ecotoxicology & Environmental Safety 32(3): 280-288.

Lemly AD (2000) Guidelines for conducting TMDL consultations on selenium. Technical Assistance Report to the U.S. Fish and Wildlife Service, Division of Environmental Contaminants, Washington, D.C.

Linares J, Linville R, Van Eennennaam J, Doroshov S (2004) Selenium effects on health and reproduction of white sturgeon in the Sacramento-San Joaquin Estuary. Final Report for CalFed Project No. ERP-02-P35, California Bay-Delta Authority, Sacramento, CA.

Lindstrom K (1983) Selenium as a growth factor for planktonic algae in laboratory experiments and in some Swedish lakes. Hydrobiologia 101:35-48.

Linville RG, Luoma SN, Cutter L, Cutter GA (2002) Increased selenium threat as a result of invasion of the exotic bivalve *Potamocorbula amurensis* into the San Francisco Bay-Delta. Aquatic Toxicology, 57(1-2): 51-64.

Looker RE, Johnson BJ (2003) Mercury in San Francisco Bay: Total Maximum Daily Load (TMDL) Project Report, San Francisco Bay Regional Water Quality Control Board, Oakland, California.

Luoma SN, Johns C, Fisher NS, Steinberg NA, Oremland RS, Reinfelder JR (1992) Determination of selenium bioavailability to a benthic bivalve from particulate and solute pathways. Environmental Science & Technology, 26: 485-491.

Luoma SN, Presser TS (2000) Forecasting Selenium Discharges to the San Francisco Bay-Delta Estuary: Ecological Effects of a Proposed San Luis Drain Extension. USGS Open FIle Report 00-0146, United States Geological Survey, Menlo Park, CA.

Maier KJ, Knight AW (1993) Comparative acute toxicity and bioconcentration of selenium by the midge Chironomus-decorus exposed to selenate, selenite, and seleno-dl-methionine. Archives of Environmental Contamination & Toxicology, 25(3): 365-370.

Maier KJ, Ogle RS, Knight AW (1988) The selenium problem in lentic ecosystems. Lake and Reservoir Management, 4: 155-163.

McKee L, Foe C (2002) Estimation of total mercury fluxes entering San Francisco Bay from the Sacramento and San Joaquin River watersheds, San Francisco Estuary Institute, Oakland, CA.

McKee L, Leatherbarrow J, Davis J, Pearce S (2002) A review of urban runoff processes in the Bay Area - Existing knowledge, conceptual model, and monitoring recommendations., San Francisco Estuary Institute, Oakland, CA.

Meseck SL (2002) Modeling the Biogeochemical Cycle of Selenium in the San Francisco Bay. Ph.D. Dissertation, Old Dominion University.

Neal RH, Sposito G, Holtzclaw KM, Traina SJ (1987) Selenite adsorption on alluvial soils: II Solution composition effects. Journal Soil Science Society America 51:1165-11169

Ogle RS, Knight AW (1996) Selenium bioaccumulation in aquatic ecosystems. 1. Effects of sulfate on the uptake and toxicity of selenate in *Daphnia magna*. Archives of Environmental Contamination & Toxicology 30(2): 274-279.

Ogle RS, Maier KJ, Kiffney P, Williams MJ, Brasher A, Melton LA, Knight AW (1988) Bioaccumulation of selenium in aquatic ecosystems. Lake and Reservoir Management 1988(4):165-173.

Ogle RS (1996) The bioaccumulation of selenium in aquatic ecosystems. Ph.D. Dissertation, University of California, Davis, CA.

Ohlendorf HM, Lowe RW, Kelly PR, Harvey TE (1986) Selenium and heavy metals in San Francisco Bay diving ducks. Journal Wildlife Management 50(1):64-71.

Ohlendorf HM, Hoffman DJ, Saiki MK, Aldrich TW (1986) Embryonic mortality and abnormalities of aquatic birds: apparent impacts of selenium from irrigation drainwater. Science of the Total Environment 52:49-63.

Ohlendorf HM (2002) The birds of Kesterson Reservoir: a historical perspective. Aquatic Toxicology 57(1-2): 1-10.

Oremland RS (1994) Biogeochemical transformations of selenium in anoxic environments. In: Frankenberger WT, Benson S (eds), Selenium in the Environment. Marcel Dekker, Inc., New York.

Oremland RS et al. (2000) Bacterial dissimilatory reduction of arsenate and sulfate in meromictic Mono Lake, California. Geochimica et Cosmochimica Acta, 64(18): 3073-3084.

Oremland, RSSJ (2000) Dissimilatory reduction of selenate and arsenate in nature. Environmental Microbe Metal Interactions

Presser TS, Barnes I (1984) Selenium concentrations in waters tributary to and in the vicinity of the Kesterson National Wildlife Refuge, Fresno and Merced Counties, California. Water Resources Investigation Report 84-4122, U.S. Geological Survey, Menlo Park, CA.

Purkerson DG, Doblin MA, Bollens SM, Luoma SN, Cutter GA (2003) Selenium in San Francisco Bay zooplankton: Potential effects of hydrodynamics and food web interactions. Estuaries 26(4A): 956-969.

Reinfelder JR, Fisher NS (1991) The assimilation of elements ingested by marine copepods. Science 251:794-796.

Reinfelder JR, Fisher NS (1994) The assimilation of elements ingested by marine planktonic bivalve larvae. Limnology Oceanography 39(1):12-20.

Reinfelder JR, Fisher NS (1997) Assimilation efficiencies and turnover rates of trace elements in marine bivalves: a comparison of oysters, clams, and mussels. Marine Biology 129:443-452.

Reinfelder JR, Fisher NS, Luoma SN, Nichols JW, Wang WX (1998) Trace element trophic transfer in aquatic organisms: A critique of the kinetic model approach. Science of the Total Environment 219:117-135.

Risebrough RW, Chapman JW, Okazaki RK, Schmidt TT (1977) Toxicants in San Francisco Bay and Estuary. Report to the Association of Bay Area Governments, Berkeley, CA.

Robinson EH, Allen OW, Poe WE, Wilson RP (1978) Utilization of dietary sulfur compounds by fingerling channel catfish: l-methionine, d,l-methionine, methionine hydroxy analogue, taurine, and inorganic sulfate. Journal of Nutrition 108:1932--1936.

Saiki MK (1986) Concentrations of selenium in aquatic food chain organisms and fish exposed to agricultural tile drainage water. Pages 25-33, in: Howard AQ (ed) Selenium in Agricultural Drainage: Implications for San Francisco Bay and the California Environment; Proceedings of the Second Selenium Symposium, Berkeley, CA, March 23, 1985. Bay Institute of San Francisco, Tiburon, CA.

Steinberg NA, Oremland RS (1990) Dissimilatory selenate reduction potentials in a diversity of sediment types. Applied Environmental Microbiology 56(11):3550-3557.

SWRCB (1994) Water quality control plan for the San Francisco Bay/Sacramento-San Joaquin Delta estuary. CA State Water Resources Control Board, Sacramento, CA.

SFBRWQCB (1992b) Mass emissions reduction strategy for selenium. San Francisco Bay Regional Water Quality Control Board, Oakland, CA.

SFBRWQCB (1998) 1998 CWA Section 303(d) List of Water Quality Limited Segments. San Francisco Bay Regional Water Quality Control Board, Oakland, CA.

SFBRWQCB (2001) Proposed revisions to Section 303(d) List and priorities for development of total maximum daily loads (TMDLs) for the San Francisco Bay region. Staff Report. San Francisco Bay Regional Water Quality Control Board, Oakland, CA.

SFBRWQCB (2002) 2002 CWA Section 303(d) List of Water Quality Limited Segments. San Francisco Bay Regional Water Quality Control Board, Oakland, CA.

San Francisco Estuary Project (1992) Comprehensive Conservation and Management Plan, Association of Bay Area Governments, Oakland, CA.

Santa Clara Valley Water District (1994) Copper and selenium in the water supply of the Santa Clara Valley, San Jose, CA.

Schlekat CE, Dowdle PR, Lee BG, Luoma SN, Oremland RS (2000) Bioavailability of particle-associated Se to the bivalve *Potamocorbula amurensis*. Environmental Science & Technology 34(21):4504-4510.

Schlekat CE, Lee BG, Luoma SN (2002) Assimilation of selenium from phytoplankton by three benthic invertebrates: effect of phytoplankton species. Marine Ecology Progress Series, 237: 79-85.

Stewart RS, Luoma SN, Schlekat CE, Doblin MA, Hieb KA (2004) Food web pathway determined how selenium affects aquatic ecosystems: A San Francisco Bay case study. Environmental Science Technology 38:4519-4526.

Tanji K, Lauchlii A, Meyer J (1986) Selenium in the San Joaquin Valley. Environment 28(6):6-11, 34-39.

Taylor KA (1997) Selenium in the Bay Environment - an overview of the environmental concerns, regulatory history, and current status, San Francisco Bay Regional Water Quality Control Board, Oakland, California.

Teh SJ, Deng X, Deng DF, Teh FC, Hung SS, Fan TW, Liu J, Higashi RM (2004) Chronic effects of dietary selenium on juvenile Sacramento splittail (*Pogonichthys macrolepidotus*). Manuscript.

United States Bureau of Reclamation (2002) Fact Sheet: San Luis Drain Feature Re-evaluation - Historical Perspective, United States Bureau of Reclamation, Sacramento, CA.

US EPA (2004) Draft Aquatic Life Water Quality Criteria for Selenium - 2004. EPA-822-D-04-001, US Environmental Protection Agency, Office of Water, Washington, D.C.

United States Environmental Protection Agency (2003) IRIS Database, Department of Homeland Security, Washington, DC.

Urquhart K, Regalado K, Carlson J, Hofmann PS, Puckett L, Wernette FG, White JR (1991) Selenium verification study 1988-1990. California Dept. of Fish and Game, Bay-Delta Project, Stockton, CA.

Vandermeulen H, Foda A (1988) Cycling of selenite and selenate in marine phytoplankton. Marine Biology 98:115-123.

Vanderveer WD, Canton SP (1997) Selenium sediment toxicity thresholds and derivation of water quality criteria for freshwater biota of western streams. Environmental Toxicology & Chemistry 16(6): 1260-1268.

Wang WX, Fisher NS, Luoma SN (1995) Assimilation of trace elements ingested by the mussel *Mytilus edulis*: effects of algal food abundance. Marine Ecology Progress Series 129:165-176.

Wang WX, Fisher NS, Luoma SN (1996) Kinetic determinations of trace element bioaccumulation in the mussel *Mytilus edulis*. Marine Ecology-Progress Series 140(1-3): 91-113.

Wang WX, Fisher NS (1998) Excretion of trace elements by marine copepods and their bioavailability to diatoms. Journal Marine Research 56:713-729.

Wang WX, Fisher NS (1999) Delineating metal accumulation pathways for marine invertebrates. Science of the Total Environment 2337/238:459-472.

Wang WX (2001) Comparison of metal uptake rate and absorption efficiency in marine bivalves. Environmental Toxicology and Chemistry 20(6):1367-1373.

Wanger O (2000) Firebaugh Canal Co. V. United States.

Watson D, et al. (1998) Spatial and Temporal Trace Level Monitoring Study of South San Francisco Bay, National Water Quality Management Council 1998 Conference, Reno, Nevada.

Wheeler AE, Zingaro RA, Irgolic K (1982) The effect of selenate, selenite, and sulfate on the growth of six unicellular marine algae. Journal Experimental Marine Biology and Ecology 57:181-194.

White JR, Hofmann PS, Hammond D, Baumgartner S (1987) Selenium verification study - 1986: A report to the California State Water Resources Control Board from the California Department of Fish and Game. California Dept. of Fish and Game, Bay-Delta Project, Stockton, CA.

White JR, Hofmann PS, Hammond D, Baumgartner S (1988) Selenium verification study - 1986-1987: A report to the California State Water Resources Control Board from the California Department of Fish and Game. California Dept. of Fish and Game, Bay-Delta Project, Stockton, CA.

White JR, Hofmann PS, Urquhart KAF, Hammond D, Baumgartner S (1989) Selenium verification study - 1987-1988: A report to the California State Water Resources Control Board from the California Department of Fish and Game. California Dept. of Fish and Game, Bay-Delta Project, Stockton, CA.

Williams MJ, Ogle RS, Knight AW, Burau RG (1994) Effects of sulfate on selenate uptake and toxicity in the green alga *Selenastrum capricornutum*. Archives of Environmental Contamination & Toxicology, 27(4): 449-453.

Woock SE, Garrett WR, Partin WE, Bryson WT (1987) Decreased survival and teratogenisis during laboratory selenium exposures to bluegill, *Lepomis macrochirus*. Bulletin Environmental Contamination and Toxicology 39:998-1005.

Wrench JJ (1978) Selenium metabolism in the marine phytoplankters *Tetraselmis tetrahele* and *Dunaliella minuta*. Marine Biology 49:231-236.

Wrench JJ, Campbell NC (1981) Protein-bound selenium in some marine organisms. Chemosphere 10:1155-1161.

Wrench JJ, Measures CI (1982) Temporal variations in dissolved selenium in a coastal ecosystem. Nature 299:431-433.

Xu Y, Wang WX, Hsieh DPH (2001) Influences of metal concentration in phytoplankton and seawater on metal assimilation and elimination in marine copepods. Environmental Toxicology and Chemistry 20(5):1067-1077.

Zawislanski PT (2003) Selenium Loads to South San Francisco Bay, California, LFR - Levine Fricke, Oakland, CA.

Zehr JP, Oremland RS (1987) Reduction of selenate to selenide by sulfate-respiring bacteria: experiments with cell suspensions and estuarine sediments. Applies Environmental Microbiology 53(6):1365-1369.

Zhang GH, Hu MH, Huang YP (1990) Se uptake and accumulation in marine phytoplankton and transfer of Se to thee clam *Puditapes philippnarum*. Marine Environmental Research 30:179-190.

Zhang Y, Moore JN (1997) Interaction of selenate with a wetland sediment. Applied Geochemistry 12:685-691.

Appendix A

Timeline of events relevant to the Clean Estuary Partnership and important selenium management issues in San Francisco Bay

Date	Event	Reference
1960	Federal San Luis Act Authorizes Construction of the San Luis Unit of the CVP, providing irrigation water for 700,000 acres in the western San Joaquin valley	(United States Bureau of Reclamation, 2002)
1967	California's Porter-Cologne Water Quality Control Act signed into law by Edmund Brown	
1968 – 1975	Construction of 83 miles of the San Luis Drain (SLD) and Kesterson Reservoir to provide drainage and temporary storage for agricultural tailwaters	(United States Bureau of Reclamation, 2002)
1972	Congress overrides Richard Nixon's veto to pass the Federal Clean Water Act on October 18, 1972.	David
1975	Construction of SLD halted pending determination of final point of discharge	(United States Bureau of Reclamation, 2002)
1975 – 1979	Kesterson Reservoir functions as an evaporation facility, resulting in elevated concentrations of selenate and bacterially mediated conversion to selenite, oganoselenide, and particulate selenium on a waterway in the path of birds migrating along the Pacific Flyway.	(United States Bureau of Reclamation, 2002); (Ohlendorf, 2002)
1983 – 1985	Studies conducted by USFWS and CDFG to assess effects of agricultural drainwater on Birds of Kesterson Reservoir; deaths and significant deformities linked to selenium bioaccumulation.	(Ohlendorf, 2002)
1985	SWRCB orders USBR to clean up and abate conditions at Kesterson Reservoir.	(United States Bureau of Reclamation, 2002)
1987	CDFG finds high selenium levels in scoters and scaup from Suisun Marsh.	(Taylor, 1997)
1989	Greg Cutter publishes peer-reviewed manuscript demonstrating that oil refineries are substantial source of selenite to the Bay,	(Cutter, 1989)
1987 – 1990	SFRWQCB requires refineries to conduct selenium source investigations and reduction measures through generic provisions in NPDES permits.	(Taylor, 1997)
1986 – 1990	CDFG conducts Selenium Verification Studies.	(Urquhart et al., 1991); (White, 1988; White, 1989)
1991	SFRWQCB imposes 50 µg/L effluent limits and performance-based mass limits on oil refineries, with compliance schedule of 3 years. Refineries appeal decision to SWRCB; appeals dismissed without prejudice.	(Taylor, 1997)
1991	SWRCB adopts Enclosed Bays and Estuaries Plan, including water quality objectives of 71 µg/L for salt water and 5 μg/L for fresh water.	(Taylor, 1997)
1992	USEPA promulgates 5 μg/L selenium criterion for all of San Francisco Bay	(Taylor, 1997)
1992 – 1994	SFRWQCB conducts public hearings to consider Basin Plan Amendments (BPA) for site specific objectives (BPA) and iterative management plans.	(Taylor, 1997)

Date	Event	Reference
1991 – 1993	Refineries sue SFRWQCB, challenging scientific basis of effluent limits and feasibility of imposed compliance schedule.	(Taylor, 1997)
1994	Refineries reach settlement agreement with SFRWQCB; settlement includes time schedule for compliance with effluent limits and agreement to pay $2 million into a selenium fund for development of mitigation and pollution studies. Settlement and subsequent Regional Board Order do not use the word "penalty"	(Taylor, 1997)
1991 – 1994	Environmental groups sue a refinery for violation of interim permit limit established by SFRWQCB, resulting in settlement consistent with SFRWQCB's effluent limits and time schedule. A second coalition of environmental groups sues two refineries on the grounds that the 1994 settlement did not impose a penalty.	(Taylor, 1997)
1998	SFRWQCB Lists all segments of San Francisco Bay as impaired due to selenium	(San Francisco Bay Regional Water Quality Control Board, 1998)
2000	U.S. District Court rules that USBR must fulfill its obligation to provide adequate drainage to San Luis Unit, consistent with 1960 San Luis Act as mandated by congress	(Wanger, 2000)
2000	USGS completes analysis forecasting of ecosystem impacts of extension of San Luis Drain	(Luoma and Presser, 2000)
2001	USBR issues reclamation plan of action in compliance with Wanger ruling.	(United States Bureau of Reclamation, 2002)
2002	SFRWQCB Lists additional 5 segments of San Francisco Bay as impaired due to selenium	(San Francisco Bay Regional Water Quality Control Board, 2002)
2002	USEPA releases Draft Aquatic Life Water Quality Criteria for Selenium, proposing fish whole-body tissue selenium criteria of 7.9 μg/g dry wt.	US EPA 2002
2002 (May)	San Francisco Bay Clean Estuary Partnership submits comments to CALFED Ecosystem Restoration Program RFP process on basis for selenium monitoring at Big Break / Marsh Creek / Dutch Slough restoration project and supporting proposals on pilot treatment of selenium in agricultural tailwaters.	Freitas, 2002

Date	Event	Reference
2002 (November)	After resource agency consultations, USEPA Notifies USFWS and NMFS of intent to develop wildlife criteria for selenium for promulgation in the California Toxics Rule	November 20, 2002 Letter from C. Kuhlman to S. Thompson and R. Lent
2002 (December)	In-valley disposal selected as preferred alternative in preliminary CEQA / NEPA analysis of drainage alternatives by prepared by USBR in compliance with Wanger ruling. This possibly eliminates the threat of severely increased selenium loadings from extension of the SLD.	(United States Bureau of Reclamation, 2002)
2004 (June)	USBR Scheduled to complete draft EIS report on drainage plan	(United States Bureau of Reclamation, 2002)
2004 (September)	USEPA to publish fish-tissue criteria document in Federal Register	
2004 (December)	Interagency working group to develop draft fish-tissue based wildlife criteria values for CTR	November 20, 2002 Letter from C. Kuhlman to S. Thompson and R. Lent
2004 (December)	Public hearings schedules on USBR draft EIS report on drainage plan	(United States Bureau of Reclamation, 2002)
2005 (June)	USBR scheduled to complete final documents and ROD on drainage plan	(United States Bureau of Reclamation, 2002)
2005 (June)	San Francisco Bay Clean Estuary Partnership develops an impairment assessment and conceptual model report for selenium in SF Bay	Abu-Saba and Ogle, 2005 (This report)
2005 (September)	Completion of external technical peer review of wildlife criteria	November 20, 2002 Letter from C. Kuhlman to S. Thompson and R. Lent
2005 – future	Implementation of USBR drainage plan for the San Luis Unit of the CVP	(United States Bureau of Reclamation, 2002)
2006 (December)	EPA Proposes changes to the CTR for wildlife criteria	November 20, 2002 Letter from C. Kuhlman to S. Thompson and R. Lent